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A Summary of Current Program 7/1/67

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and Preliminary Report of Progress

for 7/1/66 to 6/30/67

WESTERN UTILIZATION RESEARCH AND

DEVELOPMENT DIVISION

of the

AGRICULTURAL RESEARCH SERVICE

UNITED STATES DEPARTMENT OF AGRICULTURE

and related work of the

STATE AGRICULTURAL EXPERIMENT STATIONS

This progress report is primarily a tool for use of scientists and administrators in program coordination, development and evaluation; and for use of advisory committees in program review and development of recommendations for future research programs.

The summaries of progress on USDA and cooperative research include some tentative results that have not been tested sufficiently to justify general release. Such findings, when adequately confirmed, will be released promptly through established channels. Because of this, the report is not intended for publication and should not be referred to in literature citations. Copies are distributed only to members of Department staff, advisory committee members and others having a special interest in the development of public agricultural research programs.

This report also includes a list of publications reporting results of USDA and cooperative research issued between July 1, 1966 and June 30, 1967. Current agricultural research findings are also published in the monthly USDA publication, Agricultural Research. This progress report was compiled in the Western Utilization Research and Development Division, Agricultural Research Service, U.S. Department of Agriculture, Albany, California.

UNITED STATES DEPARTMENT OF AGRICULTURE

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TABLE OF CONTENTS

	Page
Introduction	iii
Area No. 1 Wheat Utilization - Food	1
Area No. 2 Wheat Utilization - Feed	18
Area No. 3 Rice Utilization - Food	20
Area No. 4 Forage Utilization - Feed	23
Area No. 5 Wool and Mohair Utilization	30
Area No. 6 Citrus and Subtropical Fruit Utilization - Food	42
Area No. 7 Deciduous Fruit and Tree Nut Utilization - Food	52
Area No. 8 Potato Utilization - Food	69
Area No. 9 Vegetable Utilization - Food	75
Area No. 10 Safflower, Castor, and Other Western Oilseeds Utilization - Food	92
Area No. 11 Safflower, Castor, and Other Western Oilseeds Utilization - Feed	96
Area No. 12 Safflower, Castor, and Other Western Oilseeds Utilization - Industrial Products	99
Area No. 13 Poultry Utilization - Food	105
Area No. 14 Egg Utilization - Food	110
Miscellaneous Publications - USDA and Cooperative Programs	117
Line Project Check List	119

This report summarizes the current program and progress during FY 1967 on research conducted at the Western Utilization Research and Development Division (one of four Utilization Divisions in the Agricultural Research Service). A few of the more significant recent accomplishments are described.

Research Area Covered by this Report

Utilization research in agriculture deals with the discovery and development of new and improved products from farm crops and the invention or perfection of processing technologies. The scientists, engineers, and technologists who carry on this research devote much of their effort to basic studies of physical and chemical properties of agricultural commodities and products derived from them, in order to provide a firm base of exact knowledge for applied developments.

The following research problem areas are within the scope of the Western Utilization Research and Development Division: (1) new and improved fruit and vegetable products; (2) new and improved food products from field crops; (3) new and improved feed and industrial products from field crops; (4) new and improved poultry meat and egg products; (5) new and improved products from wool and mohair; (6) expansion of foreign markets for U.S. farm produce; (7) protection of food supplies from harmful microorganisms and naturally occurring toxins; and (8) alleviating soil, water, and air pollution.

The farm commodities dealt with in this report are the cereal grains, wheat, rice, and barley; alfalfa and other forage crops; wool and mohair; citrus, sub-tropical, deciduous and other fruits; tree nuts; potatoes, dry beans and peas and other vegetables; castor and safflower; and poultry and eggs. Some phases of research on certain of these commodities are pursued in Utilization Research Divisions other than the Western Division: The Northern Division does research on industrial uses of wheat and on milling technology. The Eastern Division has research programs on deciduous fruits and on potatoes and other vegetables. The Southern Division carries out particular lines of research on rice, vegetables, and fruits.

Pharmacological research for all four Utilization Research Divisions is conducted at the Albany laboratory of the Western Division, and is described in the report as it applies to various subject areas. (Progress on commodities assigned to other Divisions should be found in their reports.)

Aims of Research on These Commodities

The commodities discussed here include a group that provides the nation with more than half of its food, either directly (cereal grains, fruits and vegetables, and poultry meat and eggs) or indirectly through feeding of meat animals (forage crops, wheat, barley). The remaining commodities--the non-food ones--supply us with our most important animal fibers (wool and mohair), or offer opportunities to develop numberless industrial products (castor, safflower, and other oilseeds).

The general aim of utilization research on both of these two broad categories of farm commodities is essentially the same--to provide better and less expensive products for the consuming public and to broaden and extend markets for the commodities, and thereby help to stabilize or increase the demand for them to the betterment of producers and processors.

The fundamental justification for carrying on a publicly supported program of utilization research on food products follows a somewhat different line of reasoning than does the justification for research to extend the utilization of non-food commodities. Research on the processing of farm products for food is justified primarily by its direct benefit to the entire population through improved nutrition and well-being, reduced economic loss from spoilage and waste, and increased opportunity to find profitable markets abroad. Indirectly, too, advances in technology through food processing research bring about major and desirable shifts in the commodity supply-and-demand picture for the country as a whole, as for example in the economical conversion of abundant feed grains into poultry which is marketable in refrigerated or frozen form throughout the nation and overseas.

Justification for research on non-food products, on the other hand, is based on the avowed public policy of assisting farmers threatened with loss of markets as a result of the swift rise of non-agricultural synthetics, as in the case of wool growers, or on the possibility of developing demand for presently minor crops to the point where they can be grown profitably on a large scale in order to provide cash crops for diversification and rotation programs and to remove some of the pressure of surplus from other crops--for example, safflower and castor which take land out of cotton production in the western states.

Organization of the Division

Research and development along these diverse lines are carried on for the Western Division by a staff headquartered in the Western Regional Research

Laboratory, Albany, California. A smaller Department-owned laboratory is operated in Pasadena, California, and additional laboratory space for two scientists is provided by arrangement with California Institute of Technology. Laboratory space and facilities in Puyallup, Washington, are utilized through a cooperative arrangement with Washington State University, Institute of Agricultural Sciences; and laboratory space and facilities in Honolulu, through a cooperative arrangement with the University of Hawaii.

The Albany research staff is organized into six commodity-oriented Laboratories (Cereals, Field Crops, Fruit, Poultry Products, Vegetables, and Wool and Mohair), two functional Laboratories (Pharmacology, and Engineering and Development), and a Pioneering Laboratory concerned with basic studies of plant enzymes. The staff at Pasadena is organized as the Subtropical Fruit Laboratory. The Western Regional Research Laboratory at Albany also houses the Division Director's staff, the staff required for Administrative support of the Division, and that responsible for Plant Management--that is, operation of the buildings, facilities, and grounds.

Division scientists and engineers not only conduct or supervise research in their own experimental facilities, but also greatly extend the scope and influence of their work by planning and supervising developmental activities carried on by cooperating private firms, processor organizations, or industry groups, and by arranging for research by well-qualified scientists elsewhere under research contracts and grants. In addition, certain grants of research funds are placed with investigators in foreign countries; the cost of these foreign research efforts on behalf of American agricultural interests is borne by Public Law 480 funds.

Examples of Recent Accomplishments of the Western Utilization Research and Development Division

New Food-Protein Concentrates from Wheat Now Available. Major flour milling companies are producing a new type of protein-rich concentrate for use in foods. Based on Department research, the new products are derived from byproduct fractions normally disposed of in animal feeds at low returns. In the form of finely powdered materials they are being offered for use in such products as baked goods, ready-to-eat breakfast cereals, and high-protein products for food aid programs overseas. Initial government procurements are being made of two products. One will contain the new concentrate in pre-cooked form as part of a blend of ingredients comprising a beverage for youngsters. The other is a protein-enriched flour for Asiatic baked products. The new concentrates are light amber in color and mild in flavor. They contain 20 to 35% protein which has at least 4% of the

scarce amino acid lysine. More than a million tons of food-grade concentrate can be produced per year, and nearly as much of a lower quality product will be available for use as an upgraded poultry-feed ingredient,

WURLD Wheat Under Test. WURLD Wheat, a product developed by Department scientists, is being evaluated by several commercial companies for sale in Asiatic markets. The name WURLD Wheat is applied to a light-colored quick-cooking bran-free wheat in either whole kernel or cracked form. The process consists of coating the wheat with an alkaline solution, washing the bran off in a turbulent water stream, rinsing the surface with acetic acid, and drying the product. The result is a dense, durable, stable kernel that cooks quickly.

One United States company experienced in marketing in Asia is testing the product on Guam, and another company is testing it in a number of South American and Asiatic markets, including Japan and India. All of these efforts are directed entirely at the cash, not the donation, outlet. Two plants in the United States are ready to produce WURLD Wheat, and two Philippine millers are anxious to begin production using wheat from the United States.

More Efficient Rice Drying. Department scientists have helped the California rice drying industry handle nearly twice the drying load of a decade ago. The practice of harvesting rice at higher moisture contents than before accounts for much of this increase in drying load. Utilization research showed that increasing the air temperatures and shortening the tempering periods between multiple passes in the columnar drier could speed up the process with no loss of milling quality. Recently, department scientists developed more accurate, simplified control methods. In 1966 they tested the methods under field conditions in cooperation with industry and the California State Agricultural Extension Service and Experiment Station. By increasing air temperature, drying efficiency was increased, boosting the capacity of existing driers almost 40%. The majority of California rice driers will use the improved procedures for the 1967 harvest season. Annual savings in drying costs and the increase in milling yield that are now possible reach nearly \$2 million per year.

New Process Leads to First Commercially Available Supergrade Alfalfa. Cooperative work of Department scientists with Nebraska State Department of Agriculture and industry led to development of a process for separating the fibrous fraction from the high-protein fraction of alfalfa after dehydration. The process is based on a differential grinding step whereby the leaf is reduced in particle size while the tougher stem is left in relatively large particles. This step is followed by screening or air

classification to produce a high-xanthophyll, high-protein product for poultry rations and a high-fiber fraction for ruminants. Based on this work, the first 25%-protein alfalfa product ever to be made commercially available has recently been announced by a major alfalfa dehydrating company. Many other firms are expected to follow suit during the coming year. The two standard grades of alfalfa meal contain at least 17% and 20% protein. The new product is richer in all nutrients measured than the standard grades and is better suited for poultry because of its greatly reduced fiber content.

Durable-Press Machine-Washable Wool Blend Apparel Commercialized. Commercial production of true "no-iron" dress slacks made from wool-blend fabrics was inaugurated recently. Department scientists paved the way for this development through studies of blends of settable non-wool fibers with wools made shrink resistant by the WURLAN treatment. The finished garment receives a durable-press treatment. Wool-blend slacks made this way can be machine washed repeatedly and tumble dried. Not even touch-up ironing is needed. In addition to outstanding washability, the fabric retains the aesthetics, warmth and resilience of wool. In various weaves, the new wool-blend fabrics are comfortable to wear and exhibit outstanding shape retention, crease retention and wrinkle-resistant properties.

Improvements in WURLAN Processing of Wool. Department scientists have improved the conditions of WURLAN treatment and have found that a newly available cheap solvent may be used to achieve a more than 20% reduction in chemical costs, more effective shrinkproofing, softer handle for the treated fabrics, improved stability of the reactant baths, and simplification of process control. The highly promising laboratory results obtained with worsted-type fabrics are attracting increased industrial interest, and steps are being taken to adapt these improvements to commercial processing of wool.

Basic Advances Made in Knittability of Worsted Yarn. Department scientists have provided an entirely new approach to the design of more efficient knitting machinery that will result in better knit garments as well as lower processing costs. The breakthrough resulted from a comprehensive study of the dynamics of knitting worsted-type wool yarns which revealed the complex nature of forces involved in transforming yarns into the characteristic knitted loop configuration. The interrelationships of yarn frictional properties, yarn-metal friction, yarn irregularities, and the shape of knitting cam assemblies led to equipment design and methods of operation that can maximize knitting efficiency of worsted wool yarn.

The development will lead to production of superior wool knit goods at about half the knitting cost.

Non-Bitter Precursor Responsible for Bitterness of Citrus Juices. A long-standing problem of juice manufacture from certain citrus fruits, particularly navel oranges, is the development of bitterness in the juice after extraction. When first prepared, the juice is not bitter, but bitterness gradually develops. It has been known for many years that the source of the bitter taste is the intensely bitter compound limonin, but how the limonin is produced has remained unknown. This has made attempts to develop methods to reduce bitterness in navel orange juice more difficult. Now Department research has shown that delayed bitterness results from the conversion of a non-bitter precursor to limonin after juice extraction. The precursor has been extracted from fruit tissues and identified. Freshly prepared non-bitter navel orange juice was shown to contain the non-bitter precursor, but no limonin. After heating to speed development of bitterness, a portion of the same juice was shown to contain limonin, but no precursor. Conversion of the precursor to limonin is catalyzed by juice acids and heat. The precursor has also been found in the peel portions of navel oranges and grapefruit. This new knowledge of the chemistry of delayed bitterness should lead to a process for producing non-bitter juices.

Aroma Compounds in Delicious Apple Identified. Concentrates of the volatile compounds naturally present in fruit are used for flavoring jams, jellies, and other food products. Their value depends upon their odor strength and the degree to which they retain the natural aroma of the fruit.

In the past, no objective method has been available for measuring either of these characteristics. Department scientists have now identified 50 of the volatile compounds from Delicious variety apples and have shown which ones make important contributions to aroma. Different components contribute different facets of the total aroma: one has a fully ripe or overripe odor, others add a green-apple note. By determining the concentrations of the various compounds, one can now tell both the total strength and the quality of the aroma. Industry will be able to use such analyses for product quality control, for selecting raw material of superior aroma, and even for breeding more flavorful varieties and strains of apples.

New European Markets for Dried Fruit. The market for dry prunes in Europe is widening as the result of Department efforts. Agricultural Research Service scientists, in cooperation with the Dried Fruit Association of California and the Foreign Agricultural Service, have recently obtained approval from the West German government for the use of potassium sorbate on prunes to

a maximum tolerance of 500 ppm. Heretofore, dried fruit containing this preservative could not be sold in West Germany. The demonstration that sorbate at this concentration is not detrimental and should therefore be permissible in foods should substantially assist in building markets for the United States dried fruit industry.

The process, developed by Department scientists, for applying potassium sorbate to preserve high-moisture dried fruits is widely used to treat both prunes and figs in domestic markets. The total value to the industry of the sorbate treatment of prunes alone is estimated at approximately \$7 million annually.

Non-Setting Ground Raisins. When raisins are ground and held at room temperature for just a few days, they "set" into a hard mass. Department scientists have developed an extremely simple and economical process to cope with this problem. Ground raisins, or whole raisins before grinding, are exposed to high heat for a few seconds which retards or prevents subsequent setting. This process is now in commercial use. By mid-1967, one company had produced 1/2 million pounds. A whole line of new ground raisin products, mainly for remanufacture and bakery use, is in the planning stage. These new products should greatly increase the marketability of raisins.

Frozen, Quick-Cooking Beans. A process for preparing quick-cooking (10 to 15 min) frozen products from dry beans was developed by Department scientists, supported in part by the California Lima Bean Advisory Board. The cooked beans have natural flavor and excellent appearance. The new products provide consumers with a new type of economical, high-protein, convenience food. Processors can utilize stable, low-cost raw materials; be independent of crop location and harvest time; and utilize surplus space, time and equipment. Products can be produced on demand, minimizing warehousing and transportation costs. Pilot plant production of frozen bean products has been initiated by a leading frozen food processor.

Discovery of Color Precursor Leads to New Recovery Processes for Safflower Seed Oil. Several years ago breeding work on safflower produced new, thin-hull varieties that yield up to 25% more oil than the commercially used Gila seeds. Oil extracted from the thin-hull varieties, however, was not acceptable because of its dark color which could not be removed sufficiently by standard refining procedures. Research by Department scientists has now shown that the dark color is formed from a colorless precursor which is extracted with the oil from the kernel portion of the seed. It condenses to a dark pigment during processing when temperatures are above 100° C. The color precursor, but not the pigment itself, can be removed from the oil by extraction with water or alkali.

These findings have led to three different laboratory processes for thin-hull safflower seeds, yielding oil that is free of dark color and precursor. No serious difficulties are anticipated in developing a commercial-scale process that will make thin-hull varieties usable and bring advantages to the grower, processor, and consumer. In addition, a microtest developed for detecting the color precursor in safflower seeds may help plant breeders produce new high-oil safflower varieties free of color precursor.

Superior Foam Plastics from Castor Oil. Semi-commercial scale preparation and evaluation of castor oil-based rigid urethane foams has been completed by cooperation with industry, using formulations based on those developed by Department scientists. These foams have great potential for use in structural panels and as a superior insulating material. Low-cost castor oil-based foams appear particularly well suited for spray-on applications where adhesion and foam quality are excellent and in the increasingly popular "froth" applications where use of a lower boiling blowing agent reduces problems due to exothermic heat build up and shrinkage. These findings should win for castor oil a larger share of the 200 million pounds per year market (1970 estimates) for rigid urethane foams.

Freeze-Drying of Poultry Meat. The fundamental rate-limiting processes in freeze drying of poultry meat have been satisfactorily explained by a mathematical model based on the notion that a continuous ice front retreats uniformly to the center of the piece. Heat is transferred by conduction from the surface to the ice front. Water vapor liberated at the ice front moves to the surface of the piece, partly by diffusion and partly by mass flow. Under good vacuum conditions, heat transfer is the rate-limiting factor, and at higher pressures, it is mass transfer.

The model also permits calculation of the effects of adding different gasses to the system. Under helium at a pressure of 5 mm of mercury, heat transfer to the ice surface is greatly improved without a decrease in mass transfer of water vapor away from the ice.

These studies were conducted under contract at the University of California at Berkeley. The results are being applied in work under way to reduce the time and cost of freeze drying poultry meat.

Examples of Recent Accomplishments of the State Agricultural Experiment Stations

Performance of egg yolk solids. Addition of carbohydrates to liquid egg yolk prior to spray drying affects foaming power and fat availability.

Iowa food scientists investigated the mechanism underlying these interactions by the use of commercial-type mixtures of carbohydrates and egg yolk, and by model systems composed of various carbohydrates and purified egg yolk components. Low-density lipoproteins, isolated by preparative ultracentrifugation, exhibited functional properties similar to native egg yolk. These lipoproteins are believed to play an important role in egg yolk functional performance. It is proposed that carbohydrate molecules replace the water of hydration, thereby stabilizing the lipoprotein micellar structure during drying and thus prevent release of foam damaging lipid.

Emulsifying ability of poultry meat. Interest in further processing of poultry products has lead New York (Cornell) scientists to investigate the emulsifying properties of meat obtained from the various parts of fowl, fryer-roosters and turkeys. Parts were analyzed for collagen content and used to prepare basic meat emulsions. The emulsion was evaluated by determining the volume of oil required to break it. The collagen content of poultry meat was found to give an excellent estimate of its emulsifying capacity. Breast and thigh muscles were shown to have a higher emulsifying capacity than gizzard, heart and skin. Light fowl had the poorest emulsifying properties of all meat.

Shelf-life of broilers related to composition. Georgia food researchers have shown that the level of unsaturated fatty acids and, consequently, the development of rancidity in broiler tissues can be controlled by (a) dietary factors such as protein level, type of added fat and anti-oxidant level; (b) method of packaging; and type of product fabricated from the poultry meat. The fat accounts for from 10 to 20 per cent of the total weight of uncooked broiler meat. A part of this fat is composed of certain phospholipids which have been found to contain high quantities of unsaturated fatty acids.

Replica-plating technique for food bacteria. A replica-plating technique was developed to obtain a rapid quantitative examination of the viable microbial flora on foods during storage. Experiments on milk and milk products disclosed the level and type of initial population and the rate and development of the various bacterial types during storage. Treatment of the food with heat or chemicals introduced a selective factor. The extent to which one or more groups of microorganisms participated in the terminal spoilage pattern depended on the initial level of viable population, the relative resistance to the treatment and the ability to grow under the condition of storage. Texas researchers report that this information, coupled with knowledge of the biochemical characteristics

of these species, may be used to predict shelf life, possible spoilage pattern and potential hazards to public health.

Sorption properties of dehydrated apple and potato. The method of drying apple and potato affects the rate of sorption of water of the dehydrated product. The effects of three different methods of drying on the sorption properties of dehydrated apple and potato were studied by New York food researchers. The freeze-dried products absorbed more water vapor than the puff-dried and air-dried materials. The apparent diffusivity of water vapor was considerably higher in the freeze-dried samples than in the air-dried materials. Puff-dried samples had an intermediate diffusivity value.

Respiration of potato tubers. Many suggestions have been made for the mechanism of reducing sugars accumulation during storage of potato tubers at low temperature. Massachusetts food scientists conducted experiments designed to determine whether a decrease in mitochondrial activity might account for the decrease in respiratory activity with accompanying sugar accumulation in White Rose potatoes. Mitochondria isolated from potatoes stored at 55°F were assayed. In contrast to whole tubers, mitochondrial respiration followed normal kinetics; oxidation of succinate had an apparent energy of activation of 14,000 calories. It appears that respiratory potential of the mitochondria would not limit whole tuber respiration.

Computer designs machine. Confronted with the problem of how to cull bad black walnuts from good ones without cracking them open, Missouri station scientists designed with a computer a theoretical machine that worked when actually built. The walnut sorting machine was designed after determining many of the physical characteristics of the whole and cracked nuts. To the multi-million-dollar black walnut industry the big saving in tedious hand labor required to separate bad nut meats from good ones is welcome. The machine also saves the cost of handling and cracking bad nuts.

In-shell storage of macadamia nuts. Hawaii station scientists have found that in-shell storage of macadamia nuts at 1.2 per cent moisture content is better for quality retention than storage of the processed product in jars or cans. Processed products made from nuts stored for one year were of equal quality and storage stability to those processed from freshly harvested nuts. In-shell storage will permit processors to double present plant capacity by processing kernels the year around.

Texture of canned apricots. The effect of calcium and oxalate ions on texture of canned apricot halves was investigated by California scientists.

Calcium ions were found to decrease the movement of pectic materials from fruit to syrup. This might be explained by the ability of calcium ions to bridge between polygalacturonic acid units, thus producing larger molecules which bind cells together at the middle lamella. Added oxalate ions removed calcium from pectin in the cell wall, causing an increase in water-soluble pectin in the syrup and texture softening.

Protein alteration in flour damaged by milling. Overgrinding of flour affects flour quality. North Dakota scientists studied protein alteration in flour milled with varying degrees of severity by means of nonprotein nitrogen (NPN) determinations, specific color reactions, Sephadex column chromatography, gel electrophoresis, and sulfhydryl group analysis. The proteins of the water-soluble fraction were given special attention. The possibility of protein denaturation in highly damaged flour was indicated by a decrease in the total flour nitrogen contained in the water-soluble fraction. An increase in NPN in the water-solubles was observed as severity of milling increased. Two color reactions for the measurement of amino groups supported the NPN units. In addition, the water-soluble proteins produced two main peaks when separated on a Sephadex 7-50 column. Average values for several column determinations indicated a slight increase in the lower-molecular-weight protein content of the damaged flour. These data indicate an alternation of protein structure.

Fragmentation during enzymatic degradation of cellulose. The nature of cellulose breakdown in forage digestion has been explored by Virginia station scientists. They have shown with purified cellulase that the enzymes solubilize cellulose not only by erosion of the particle surfaces but also by fragmentation of the larger cellulose particles into sub-units which are still particulate. Tighter protein hydrogen bonding to cellulose has been suggested as the mechanism which breaks the cellulose hydrogen bonds formerly holding the initial micelles together,

AREA NO. 1. WHEAT UTILIZATION - FOOD

Problem. The dominant feature of the wheat economy in the United States continues to be a production capacity that can outpace consumption, including the substantially expanded foreign markets of recent years. Increased exports of wheat from the United States in the last few years have brought our wheat carryover to a level that provides less than a prudent reserve. However, the capacity to produce wheat in this country is still restricted.

We view this North American surplus capacity as an unparalleled opportunity. Wheat in excess of domestic needs can be used to buy time in the over-populated areas of the world until a self-sufficient agriculture can be developed there. Export donations and concessional sales of 600-800 million bushels per year are providing food where it is most needed in the world. This distribution of wheat serves immediate Defense and State Department missions and also stimulates a long-range market development for United States agriculture. New wheat foods specifically adapted to conditions of use in every region of the world would help materially to popularize this valuable food grain in areas where it is now virtually unknown, and development of simplified methods to process the products at the point of use would speed their adoption.

We also need to increase and maintain the commercial exports that contribute favorably to our international trade balance. New flour-maturing processes to elicit maximum quality performance of wheats and flours in products produced in Europe and Japan would help significantly to promote trade in these dollar markets. Sustained further gains in wheat markets are necessary to ease governmental restrictions on production more than they have already been eased, and especially to strengthen export trade balances. Increased world supplies of wheat and restrictive political decisions in the European Economic Community have contributed to seriously reduced commercial exports in some years. Everything possible must be done to increase total wheat markets, but especially those in which payments are made in dollars.

Consumers of wheat foods in this country have benefited greatly by introduction of a wide variety of new and improved products. Well balanced diets, reasonable food costs, and improved convenience result from such developments and are suitable objectives of research. Research programs along these lines would sustain and increase markets for wheat.

An essential foundation for a successful product and process development program is basic research on the composition of all classes of wheat and the fundamental properties of their constituents. This kind of information provides the foundation for improved and new products and processes.

USDA AND COOPERATIVE PROGRAMS

Research on utilization of wheat for food seeks to solve the most urgent problems hindering the development of markets for the full productive capacity of U.S. agriculture. The emphasis is on (1) expansion of overseas dollar markets for U.S. wheats; (2) development of new wheat food products for long-term market development in food-short nations abroad; (3) raising the domestic consumption of wheat foods by increased variety, quality, and convenience; and (4) finding means to upgrade wheat millfeeds to recover fractions of nutritious food quality. Basic research on the fundamental chemical and physical properties of wheat and barley constituents and on the functional properties of wheat flour constituents supports the product development and problem-solving segments of the program.

Research is conducted by the Western Utilization Research and Development Division at Albany, California; under contracts and grants at Chicago, Illinois; Manhattan, Kansas; Madison, Wisconsin; St. Paul, Minnesota; Menlo Park, California; and Corvallis, Oregon; and under P.L. 480 grants in England, Australia, Switzerland, Japan, and Belgium.

The Federal program of research in this area totals 23.6 scientist man-years including six contracts and grants. Of this number, 6.5 are assigned to investigations on chemical composition and physical properties; 7.7 on color, texture and other quality characteristics; 3.0 on microbiology and toxicology; and 6.4 on technology - process and product development. In addition, the Division sponsors five research grants under Public Law 480.

PROGRAM OF STATE EXPERIMENT STATIONS

A total of 14.8 scientist man-years is devoted to this area of research.

PROGRESS -- USDA AND COOPERATIVE PROGRAMS

A. Chemical Composition and Physical Properties

1. Improvement of Baking Properties of Bread Flour by Controlling Maturation. We are studying the mechanism of wheat flour maturation to determine how maturing improves the baking properties of bread flour, and to develop maturing treatments for hard red winter wheat flour which will be acceptable in all dollar export markets.

We have demonstrated that phosphatidyl serine and the water-soluble proteins of flour form protein-metal-phospholipid complexes with magnesium, calcium, cobalt, and nickel ions. The protein components so complexed are specific with regard to metal ion, but methylation of the proteins destroys this specificity. Amino acid analyses show few differences between the complexed and non-complexed proteins, although threonine plus serine content is about twice as high in the complexed protein.

Procedures were developed for solubilization and chromatographic fractionation of water-insoluble hemicelluloses into five fractions of different composition. These procedures will permit assessing their function in dough and comparing flours.

We have observed that the amount of hydrogen sulfide released by doughs mixed vigorously under nitrogen differed at least 3-fold among samples of bread wheat flours. These results suggest that hydrogen sulfide may arise from one or only a few components.

Oxidative enzymes appear to be related to the mechanism of flour aging. Under a research grant, investigations are conducted at the University of Wisconsin to determine the role of native enzyme systems of endosperm in oxidative improvement of winter wheat flours and means of enhancing favorable mechanisms. Oxidative enzymes are being studied in hard red winter wheats and in hard red spring wheats. Indole acetic acid oxidase activity was found in the winter wheats only.

The enzyme lipoxidase is responsible for oxidizing lipids which are of importance in their chemical relationships with proteins and their effects on maturation of flours and mixing quality of doughs. When the activity of lipoxidase is high, we find that mixing tolerance is low, with the result that the dough breaks down quickly. Lipoxidase measurement could become an important specification for flours. Comparative measurements of wheat and soybean lipoxidase show that wheat lipoxidase, unlike soybean lipoxidase, showed little activity on fatty acid esters; both types were equally active on free fatty acids. Soy lipoxidase catalyzed the oxidation of polyunsaturated digalactosyl diglyceride lipids but only when trace amounts of linolenic acid were present; wheat lipoxidase was inactive under these conditions. If raw soy flour is added to wheat flour (as is sometimes done commercially), enzyme-catalyzed oxidation may affect many of the lipids of wheat flour and thus the mixing tolerance of the flour.

Free radical-generating oxidases caused aggregation of soluble proteins in model systems containing the oxidase, hydrogen peroxide, a hydrogen-donor, and a soluble protein. If occurring in dough systems, this reaction could affect mixing and baking properties.

Existing analytical methods for assaying riboflavin, in its many forms, were found to be unsuitable for use with wheat or flour. Under a P.L. 480 grant, the Agricultural High School in Poznan, Poland developed methods by which riboflavins in wheat and flour could be accurately determined. Flavins were shown to cause loss of activity of amylolytic and proteolytic enzymes when exposed to light. The involvement of sulfhydryl groups in this photosensitivity phenomenon was indicated. These studies also supported the view that riboflavin may regulate the activity of amylolytic enzymes in wheat during maturation of the grain.

2. Use of Malting to Modify Wheat Proteins and Other Constituents to Improve Nutrient Value of Foods. Contract research at the University of Minnesota in St. Paul is conducted to determine the nature and extent of changes in proteins and other major constituents of wheat that occur under malting conditions selected to produce desirable alterations in flavor, texture, and nutritive properties, but with limited conversion of seed solids to rootlets or acrospire. Certified seed of 8 wheat varieties has been malted at 2 temperatures (12° and 15° C.) and dried. Analysis shows that flour proteins change only slightly as a result of malting; but bran protein changes markedly. Malting greatly increases proteolytic activity; the nature of the proteases responsible is being studied. Other analyses indicate that amino acid patterns of flour proteins change little after malting, but in the non-protein nitrogenous fraction, aspartic and glutamic acids increase greatly; and alanine, phenylalanine, leucine, serine, threonine, and valine increase moderately.

B. Flavor

1. Bread Flavors. We investigated the chemistry associated with bread flavor to find means for enhancing and stabilizing flavor so that bread and other baked products will be more satisfying and desirable for consumers. We have obtained material with a strong cracker-like odor by reacting proline with glycerol. The same reaction was also shown to take place with sorbitol, glucose, and even glycerides. Gas-liquid chromatography examination of a bread-aroma concentrate and the semi-purified fractions of the reaction mixture revealed three peaks having a cracker-like odor. The retention time of one of these peaks was identical for both substances. Subsequent examination of this material gave a presumptive identity of 1-azabicyclo(3.3.0) oct-4-one. A second peak from the bread-aroma concentrate was tentatively identified as N-methyl-2-acetopyrrolidine. No identity was established for the first of the three peaks because of inability to collect enough sample material in a satisfactory state of purity. Continuing attempts to obtain enough sample for positive identification of all three of the odor-producing substances have involved forming a complex with bisulfite to stabilize the compounds.

Although bisulfite quenches the cracker-like odor properties of the purified fractions, the reaction is reversible. The compounds appear to be unstable, even at low temperatures unless stored as bisulfite complexes. This instability is reminiscent of the transient nature of the freshly baked aroma of bread.

Attempts to improve the flavor and aroma of bread by addition of a proline-dihydroxyacetone or proline-glycerol mixture were not entirely successful. Proline alone definitely improves bread, as was established under an earlier research contract. The reaction mixture, however, produced both good and bad effects, the latter presumably because of the side reaction products. Until the purified substances can be added to breads, a comparison with the effect due to proline alone will not be possible.

2. Civil Defense Fallout Shelter Rations. Research on food supply for fallout shelters is funded by transfer from the Office of Civil Defense, Department of Defense. An accelerated storage study on puffed bulgur stored in oxygen has shown that initial rate of off-flavor development is related to an increase in carbon monoxide and hexanal. However, the initial odor change was not considered objectionable or typically rancid. Pentane appeared in detectable amounts well after the initial off-flavor development had first appeared but has not increased significantly (102 days). Since the puffed bulgur is still not considered rancid, it is possible that continued storage will show a relationship between pentane accumulation and rancidity. Concentrations of oleic, linoleic, and linolenic acids were found, within experimental error, to be the same in flour, bulgur, and puffed bulgur (18%, 50%, and 4%, respectively).

Determinations of hexanal and carbon monoxide production will be useful for objective non-destructive surveillance tests of stored shelter wafers. Further work will be required to determine whether these compounds, plus pentane, show a correlation with organoleptic rancidity development in puffed bulgur. The successful development of an objective test to judge the condition of food products also will have considerable applicability for providing consumers with products in good condition. Although developed for use with bulgur containing products, the method should be equally applicable to other fat containing foods in which linoleic acid is the principal fatty acid component of the fats. The rapid, non-destructive, and objective character of the test thus will help maintain cereal and other food consumption by assisting in providing consumers with high quality products.

C. Color, Texture and Other Quality Factors

1. Improved Quality of Baked Goods Through Study of Wheat Proteins and Their Interactions with Flour Components and Dough Ingredients. Wheat proteins are known to have a major influence on the physical and structural characteristics of doughs and baked products, but how these proteins exert their effects is not known. Therefore, in addition to investigating the composition and physical properties of proteins, we are especially interested in their interactions with other components of flour and dough.

The effect of proteins on the functional properties of wheat flour and dough is under investigation. We have found that alpha-gliadin molecules can aggregate, at pH 5 in low salt concentrations, to form soluble, high-particle-weight fibrils of a uniform width, suggesting that some rheological properties of doughs may depend on this aggregation. The fibrils have been found in acidic flour extracts and in purified alpha-gliadin solutions.

A "globulin" component of flour moves with the same high mobility in zone electrophoresis as does purothionin, a low-molecular-weight protein extracted from flour by lipid solvents. The globulin component was found to have a high cystine content and other properties characteristic of

purothionin. The apparent identity of the two components suggests that globulins may participate extensively in lipid-protein complex formation. We have devised a sensitive technique, based on simultaneous ultraviolet absorption and fluorescence monitoring, for determining the homogeneity of fractions. The method has shown the presence of five components in a preparation where either ultraviolet absorption or fluorescence used alone showed only two. This technique should be applicable to many protein isolation problems. A program to determine the relationships between dough properties and protein interactions has been initiated.

In contract research conducted at Washington State University, the fate of extractable proteins was followed by the use of radioactive tracers. Radiotracer-labeled wheat from growth chambers had an abnormal flour protein distribution very low in gliadin components. Field-grown labeled wheat was normal in flour protein distribution. Variations in nitrogen and light supply did not account for the low gliadins in growth-chamber wheat. Results from incorporation of four labeled protein fractions in flour-water doughs and fermented doughs showed only one significant change in distribution of tracer label; under-mixed flour-water doughs behaved as though lower-molecular-weight components had been formed from high-molecular-weight gluten components. Optimum- and over-mixed doughs did not show this. This result needs confirmation because it does not agree with results of other work on solubilization of dough components with mixing.

A study of proteins and lipids of spring and winter wheat flours to identify differences responsible for their differing response to oxidative maturing treatments has been concluded at Kansas State University. Pentosan preparations from a durum flour differed from those from other types of wheat in carbohydrate composition, electrophoretic mobility of associated proteins, and infrared spectra. All pentosans decreased dough-development time and dough stability. Durum pentosans lowered, but others increased or did not affect amylograph peak viscosity. Added pentosans increased oxidation requirements of doughs. Loaf volumes were increased by hard red winter and club pentosans, but decreased by soft red winter and durum pentosans.

We have concluded a study of the compositional factors of wheat flours which limit the percentage of nonfat dry milk solids which can be satisfactorily used in continuous-mix processes for bread production. We demonstrated that wheat flour contains a surprisingly active specific protease which, at slightly acidic pH, rapidly attacks the α_s -casein component of nonfat dry milk.

The presence of a protease in flour that attacks specifically α_s -casein of nonfat dry milk proteins suggested that doughs containing nonfat dry milk or α_s -casein be compared when the nonfat dry milk or α_s -casein had and had not been present in a brew together with flour. The results indicated that the action of flour protease and α_s -casein was of minor importance to continuous mix bread production. When brews contained no

flour, or only 10% flour, 6% nonfat dry milk as expected consistently caused decreases in crumb score and loaf volume. When 0.28% α_s -casein replaced 4% nonfat dry milk (which would contribute 0.28% α_s -casein), adverse effects were no longer observed. A volume increase usually was obtained, even when the α_s -casein was hydrated separately from the brew and added at the dough mixing state. With brews containing 30% flour, in contrast, α_s -casein in the brew had no effect unless hydrated separately, when it gave a small volume decrease. The decrease was not as great as that caused by the equivalent amount of nonfat dry milk however.

We made measurements of the loss of sulfhydryl groups from doughs containing nonfat dry milk during 20 minutes mixing. The addition of nonfat dry milk in amounts up to 6% of flour weight progressively reduced the loss of sulfhydryl groups, with the effect being much more marked at pH 5, about the pH of continuous-mix doughs. Above 6% nonfat dry milk, however, the trend was reversed, both at pH 5 and with pH unadjusted. Results with four flours were very similar and consistent, although absolute changes during mixing were small.

We studied the effects of nonfat dry milk on the release of hydrogen sulfide from doughs mixed under nitrogen. Three samples of nonfat dry milk were used--a high-heat commercial product for bakery use, a low-heat agglomerated product for home consumption, and a freeze-dried nonfat dry milk prepared in the lab from pasteurized skim milk. When added at 6% of flour weight to either a commercial spring or winter wheat bread flour, the high-heat nonfat dry milk doughs released more hydrogen sulfide than doughs containing the low-heat solids. The effect of 6% high-heat nonfat dry milk did not quite equal that of an additional 6% flour; but the difference between nonfat dry milk preparations was so marked that the doughs containing 6% low-heat nonfat dry milk released less hydrogen sulfide than control doughs (with no added flour or nonfat dry milk). The data suggest that the increased availability of sulfhydryl groups in high-heat, as compared to low-heat, nonfat dry milk may permit more ready incorporation of the high-heat nonfat dry milk proteins into films of flour proteins; on the other hand, the difference may reflect only a difference in water-absorbing capacity which changes dough consistency.

Illinois Institute of Technology Research Institute is conducting contract research to determine the macromolecular structures present or developed in flours and doughs to improve control of dough properties and selection of flour. Transmission electronmicrographs of dough showed large stained areas predominantly proteinaceous, which suggests that the network-type protein structure in flour had been stretched. Unaffected starch granules were present, but their original distribution relative to other components had been changed. Diffuse staining around granules suggests that doughing leaches starch components out of granules to a significant extent. In contrast to flour, dough sections show no structural organization. Scanning electronmicrographs show flour to have cleavage lines due to milling. Starch granules have smooth surfaces, with occasional patches of adhering

protein. The pervading proteinaceous matrix has rough, broken, and curled edges where it is broken up during milling. In dough, the protein is transformed into a smooth, veil-like network stretched over the starch granules. Some granules seem to adhere to the surface of the protein continuum, but others are completely enveloped.

We have initiated a program to improve the baking properties of reconstituted bread doughs by modifying wheat starch granule preparations and the adhering proteins, lipids, and hemicelluloses.

Research at Osaka Women's University, Osaka, Japan, is supported by P.L. 480 funds. In studies conducted there, the viscoelastic properties of wheat proteins are varied in an attempt to clarify the mechanism of dough-forming properties of flour. Analyses indicate that the reaction of gluten with polymers is stoichiometric with respect to the acidic groups of the polymer and the basic groups of the protein. The mode of combination may be through a salt linkage. At equal ionic levels, polyvinyl sulfate showed small and carrageenan moderate positive effects on the extensibility of dough. Increased stability, but slightly reduced consistency resulted, these modifications result in generally better dough characteristics. Sulfhydryl-chitosan and polyvinyl thioglycolate showed dough weakening similar to that due to cysteine and thioglycolic acid.

Under a P.L. 480 grant, the Centre National d'Assistance Technique et de Recherche Appliquée, Antwerp, Belgium, is conducting studies to determine the isopropanol-soluble proteins from wheat that correlate with baking quality, evaluated by European methods, and with response to improvers. Characterization of 24 wheats for 9 physico-chemical properties is completed. Ground samples were extracted and nitrogen and total solids were determined. Results indicate that the gliadin/albumin ratio is type-dependent, and variably lowered by n-butanol treatment; the gliadin/glutenin ratio does not vary with type of wheat, with or without butanol treatment. Butanol treatment reduces the amount of protein extracted with 40% isopropanol but enhances its purity and protein soluble in 40% isopropanol increases with protein content of wheat and is slightly higher in winter than in spring wheats.

A P.L. 480 grant to the Pasteur Institute in Paris, France, has been concluded. Proteins of barley and wheat were studied, with particular emphasis on immunochemical methods of analysis. Barley proteins were resolved into 17-22 constituents. Barley and malt beta-amylase were in the albumin fraction, and malt alpha-amylase in the globulin fraction. No precursor of alpha-amylase was found in ungerminated barley, and apparently the enzyme is formed de novo during germination. Alpha- and beta-amylase were purified to the point at which monospecific antisera could be prepared from them. Proteolytic activity was described and partially located among fractions. The salt-soluble wheat proteins were resolved into 10 constituents. Protease activity was richest in those components moving

most rapidly to the anode at pH 8.2. Immuno-electrophoretic analysis of 3 varieties showed only quantitative differences in protein components. The 'insoluble' wheat proteins (gliadin, glutenin) showed antigenic identity, but were electrophoretically heterogeneous. It was concluded that the insoluble proteins probably have similar sub-units and that the antigenic sub-units were linked covalently but not primarily by disulfide bonds. Phosphorylated groups were found in glutenin and gliadin.

A study of insoluble gluten by application of ultrasonic vibrations to suspensions of the protein has been concluded. The work was conducted at the National Institute of Agronomic Research in Paris, France, supported by P.L. 480 funds. A series of flours, acidic extracts of the flours, and glutens from them comprised the experimental material. Effects obtained varied with the frequency of the irradiation, and in general, effects were greater in magnitude for dispersions of gluten than for the wet gum gluten itself.

Glutens from untreated flours appeared to be partly degraded by the irradiation in that the fraction emerging first from ion-exclusion columns was diminished in quantity, but solubility and viscosity decreased. The higher frequencies used were the most effective in producing the changes. Removal of water- or salt-soluble proteins from flours before separation of glutens led to divergent effects. Results with glutens from flours without water soluble protein suggested that aggregation effects accompanied degradative effects. Glutens from defatted flours were more sensitive to the ultrasonic radiation than the gluten from untreated flour. Low- to mid-range frequencies were most effective in causing a decline in quantity of both high and low molecular weight fractions coming off ion-exclusion columns.

Under a P.L. 480 grant, the Swiss Federal Institute of Technology at Zurich, Switzerland, is studying the nature of soluble pentosans, their mode of linkage to proteins, and the role of polyphenols in forming gels from aqueous extracts of wheat flour. A highly active purified xylanase was isolated from a crude cellulase preparation. A xylanase digest of a starch-free, non-gelling pentosan fraction showed xylose, arabinose, and galactose present in the acetone-precipitated portion after acid digestion; the filtrate yielded xylose and some higher oligomeres. Viscosity of a pure arabinoxylan fraction incubated with the enzyme decreased rapidly over the first 20 min., but viscosity of flour suspensions decreased much more slowly.

Caffeic acid esters of starch were successfully prepared as models of naturally occurring polyphenolic-polysaccharide complexes. Three degrees of substitution were obtained: 30, 8, and 0.4 caffeic acids residues per 100 glucose units; the last two were water soluble. Measurements of ferulic acid in wheat flour indicate 2 esters for each 100 xylose units, if all the ferulic acid is located in the xylan portion of the glycoprotein.

The Flour Milling and Baking Research Association at Chorleywood, England, supported by P.L. 480 funds, has concluded a study of means of solubilizing gluten proteins so their component parts may be better understood. Procedures were successfully developed to solubilize the total protein of wheat flour with no apparent rupture of any covalent linkages, other than disulfide bonds. This necessitated careful adaptation of prevailing sulfitolysis procedures and use of milder than standard conditions. At pH 8.6 substantial disulfide-sulfhydryl group radical interchange was induced with low molecular weight thiols, so that effects of alterations in patterns of reactive side groups on protein properties can be studied. Limited comparison of thiol and disulfide bond accessibilities in a strong and a weak flour showed the stronger flour to respond more quickly, and to a greater extent, as urea concentrations were increased to promote accessibility. Heat denaturation of flour proteins did not alter the accessibility patterns. In confirmation of reports based on other methods, gliadin disulfide linkages were shown to be largely, if not completely, intrachain. Other flour proteins had a much greater content of interchain bonds.

Under another P.L. 480 grant, the Flour Milling and Baking Research Association in Chorleywood, England, is investigating the nature and extent of interactions between lipids and other major dough constituents and how they relate to the structure of baked goods. Six categories of lipids in doughs seem to relate to binding forces: 1) mechanically expressible, 2) non-polar-solvent extractable, 3) water-miscible, weakly polar-solvent extractable, 4) electrostatically bound, 5) metal-chelated, and 6) firmly bound (extensive polar-solvent extraction). Time of fat addition during dough mixing did not affect the proportion of free (ether extractable) and bound (water-saturated butanol extractable) lipids nor the phospholipid binding. Neither did rate of work input change free/bound lipid; total work input alone was the controlling parameter. Lipid/gluten ratios in doughs did not relate entirely to protein content of strong and weak flours. Much more lipid was associated with the starch fraction in weak flour than in strong flour. Nitrous acid treatment of flours produced no shift in free/bound lipids, but it reduced bound phospholipids. When long-chain saturated hydrocarbons were used as the fat component in doughs, loaf volumes increased with increasing chain length. The effect appeared within flours, but differed widely between flours, which indicates important flour-fat interactions and contradicts the hypothesis that improvements depend only on physical properties of fat. To study lipid protein complexes, purothionin has been prepared and characterized. A second fraction from the petroleum ether extract also shows ester and amide absorption in the infrared, indicative of the presences of other lipoproteins.

Contract research at Stanford Research Institute in Menlo Park, California is conducted to relate the molecular organization in wheat flour doughs to baking characteristics. Stress-strain data were obtained for doughs of a bread flour and of a pastry flour at several moisture levels, temperatures, and rates of extension. An equation representing the

behavior of the doughs expresses stress as a function of a material parameter and contains a strain-independent function of time, as well as a time-independent function of strain. The material parameter is the constant strain rate modulus at a suitably chosen time, at the reference temperature T_0 and reference water absorption W_0 . The time function is $(t/a_T a_W)^x$ where a_T and a_W are empirically determined shift factors which reduce to unity at the reference conditions of temperature and water absorption. With this expression, stress-strain behavior could be linearized up to extension of 180% for the bread flour, but only to about 80% for the pastry flour. The time dependence of the constant strain rate modulus also differed; for the bread flour, $x = 0.29$, for the pastry flour, -0.40 . Other differences appeared in the true stress at break and in the area under the stress-strain curves. The large deformation results show that doughs of different water contents and at different temperatures can be compared and indicate several parameters for comparison. Thus far, elastic forces appear to contribute prominently to the stress-strain behavior even though dough is readily deformed.

Supported by P.L. 480 funds, the Bread Research Institute of Australia in North Ryde, Australia is conducting research to determine viscoelastic properties of doughs, and relate the properties to behavior of doughs in current empirical instruments and in new commercial procedures. An instrument was designed to study rheological properties of doughs over a range of frequencies. Stress-relaxation behavior was derived for times as short as 0.001 second. At low strains, dough viscoelastic behavior was linear but at higher values it became increasingly non-linear. In the linear range, a temperature-frequency superposition principle was established, making possible separation of dependent variable responses by reference to a common temperature. Similarly, a water absorption-frequency superposition principle was established. Thus any given set of dough properties can be reproduced by varying the water absorption. The simplicity of these relationships suggests that variations in viscoelastic properties of gluten are modified and minimized by the large proportion of starch in doughs. Therefore, interactions of gluten and starch may be important in explaining differences among doughs.

2. Carrying Capacity of U.S. Hard Winter Wheats for European Soft Wheats in Bread Manufacture. In order to strengthen the competitive position of U.S. wheat in export markets, contract research at Kansas State University is conducted to determine and quantitate the properties of U.S. hard red winter wheat flours of value in blending with weak flours to obtain optimum baking performance. All 1965-crop wheat samples, including a Canadian wheat of 13.5% protein were milled. However, delayed receipt of European samples precluded completion of analysis. Hagberg "falling number" values were illustrative of the problems encountered with European wheats: 1964-crop flours ranged from 232 to 638 and 1965-crop from 151 to 458. Values for U.S. wheat are from 493

to 876. Low values are indicative of excessively high alpha-amylase content which is caused by sprouted grains commonly present in European wheat.

D. Microbiology and Toxicology

1. Improved Quality Retention in Frozen Fermented Doughs. We seek to increase the quality and consumer acceptance of frozen fermented doughs by determining the factors which affect the quality of frozen doughs. We prepared frozen bread dough by the straight dough method and stored it for 6 weeks at 0° F. A short fermentation time (30 minutes or less) was adequate for stability as measured by residual yeast count, gassing power, proof time and bread volume. Increasing the yeast level from the conventional 2 or 3% to 6% was of further benefit in shortening proof time. Longer fermentation times, in addition to causing poor yeast stability, also yielded weak or slack dough with poor gas-retention properties. Addition of approximately 40 ppm of potassium bromate largely corrected the weakness-of-dough defect, but was of no value in improving yeast stability or proof time.

Doughs prepared by the sponge and dough method and stored for 6 weeks at 0° F. exhibited very poor stability by all indices. Spiking with additional yeast at the second (or dough) stage was of little benefit. The following changes in procedure markedly improved stability: adding non-fat milk solids to the sponge mix, reducing the sponge time from 4 hours to 1 hour, and chilling the sponge before mixing the dough. Spiking with additional yeast at the dough stage was then of substantial benefit and, in fact, essential, when combined with one or all of the above changes.

E. Technology--Process and Product Development

1. Development of Protein-Enriched Foods from Wheat Flour and Millfeed Fractions and Concentrates. We are conducting research to develop methods for obtaining protein concentrates from millfeeds for human food. Protein concentrates prepared by various methods were compared. One protein concentrate was prepared by rollermilling and sifting of shorts at 9% moisture content. The protein efficiency ratio of this concentrate was 1.9 and lysine content was 4.2 g/16 N. Thiamine, folic acid, and choline were increased in the protein concentrate, while riboflavin, panthothenic acid, niacin, and pyridoxine were reduced. All vitamins were present at 3 to 38 times the concentration found in unenriched, white flour. High moisture content (13-15%) in shorts before milling resulted in protein concentrates of low yield and low lysine, thiamine, and riboflavin contents. At milling moistures of 9 to 11%, protein content of the protein concentrate was at a peak, fiber content was low, and yield, lysine and thiamine were all at high levels. Finer sieves produced protein concentrates that were very low in fiber, but yields were cut sharply, and the contents of thiamine, riboflavin, and lysine were lower. Various analyses suggest that endosperm and germ tissue are concentrated in the protein concentrates from shorts,

while pericarp and aleurone are reduced. Commercial germ showed a great increase in friability at 9% moisture compared with 15% moisture.

We are developing milk-like and meat-like products from native or modified wheat and wheat proteins. We have developed a new, inexpensive method for nearly complete separation of protein and starch in wheat flours with no loss of soluble solids and consequently reduced waste problems. Bread baked from the recombined protein and starch was about 15% lower in loaf volume than bread made from starting flour.

The utility in foods of protein concentrates from wheat milling by-products was shown by the development of an inexpensive, nutritious and palatable beverage product prepared by amylase digestion of a blend of the high protein and standard flours fortified with minerals. The product compares favorably with other similar low-cost products.

2. Expand Foreign Markets by Developing New Non-baked Cereal Products of Improved Quality and Nutrient Content. The world food deficit is a continuing threat to international peace and economic security. Great opportunities exist to process and distribute new food products tailored to the needs and habits of specific foreign populations, to build and sustain commercial markets and to provide acceptable foods at lowest costs.

WURLD wheat, developed at the Western Lab, is an example of these new food products. It is a whole kernel or cracked kernel product from which the bran has been removed by lye-peeling. WURLD wheat has been tested by Church World Services for acceptability in Hong Kong. The product is not objectionable to any considerable proportion of the Chinese eating it there, even though served repeatedly. It was well accepted, although less well than the very familiar foods. A similar test in Madras, India, under CARE is still unreported. A market test is to begin soon on Guam among natives of principally Filipino origin. Extensive commercial exploitation is proposed if the test results are favorable.

For the consideration of AID, we collected data on the nutritive properties of WURLD wheat. On the basis of protein quantity and water soluble vitamins, the new product ranks well above white flour--even high extraction flour--and rice. It is very slightly inferior to raw wheat or bulgur in vitamin content and protein quality.

Contract research at Oregon State University is conducted to identify compounds in wheat bran and aleurone that impart color to these tissues, as a guide to developing light-colored wheat foods. Gas chromatography studies have been initiated to quantitate reference phenolics and show complexity of the phenolic-type of compounds found earlier in bran extracts. It has been found that nitrogen occurs in a major colored bran extract.

Two other studies are being conducted to increase world food supplies. We are developing economic methods to recover protein from millfeeds to increase

the supply of edible protein. By rollermilling and sifting of shorts at 9% moisture content, we have developed a protein concentrate with a protein efficiency ratio of 1.9 low fiber content, and high levels of lysine, thiamine and yield.

Also, we are conducting research to simulate milk and meat in dry and moist forms from combinations of native and modified wheat and wheat proteins and other flavor-, texture-, and nutrition-enhancing materials for specific export and domestic markets. We have developed an inexpensive, nutritious and palatable beverage product prepared by amylase digestion of a blend of high protein and standard flours fortified with minerals.

PUBLICATIONS -- USDA AND COOPERATIVE PROGRAMS

Chemical Composition and Physical Properties

- Bur , Jean and Gay, Pierre. 1964. Flour lipids and their role in baking performance. Industries Agricoles et Alimentaires 81(3):175-183 and 81(4):275-288. 1/
- Honold, G. R., Macko, V., and Stahmann, M. A. 1967. NAD and NADP-dependent malate dehydrogenase in wheat. Naturwissenschaften 54(7):169. (Grant)
- Honold, G. R., Farkas, G. L., and Stahmann, M. A. 1966. The oxidation-reduction enzymes of wheat. I. A qualitative investigation of the dehydrogenases. Cereal Chem. 43(5):517-29. (Grant)
- Inamine, E. S., Noble, Elaine G., and Mecham, D. K. 1967. Solubilization and fractionation of wheat flour proteins insoluble in dilute acetic acid. Cereal Chem. 44(2):143-51.
- Macko, V., Honold, G. R., and Stahmann, M. A. 1967. Soluble proteins and multiple enzyme forms in early growth of wheat. Phytochem. 6:465-71 (Grant)
- Tao, Rita Pi-Chi and Pomeranz, Y. 1967. Water-soluble pentosans in flours varying widely in bread-making potential. J. Food Sci. 32(2):162-68 (Contract)

Flavor

- Horvat, R. J., McFadden, W. H., Ng, H., Lundin, R. E., Lane, W. G., and Shepherd, A. D. 1966. Identification of methyl octanoate derivatives from autoxidized methyl linoleate by mass spectrometry, nuclear magnetic resonance and infrared spectroscopy. Nature 211(5046):298-9.
- Hunter, Irving R. and Walden, Mayo K. 1966. Carbonyls from semicarbazones. Separation by gas chromatography. J. Gas Chromatog. 4(7):245-8.
- Hunter, I. R., Walden, M. K., McFadden, W. H., and Pence, J. W. 1966. Production of bread-like aromas from proline and glycerol. Cereal Sci. Today 11(11): 493-494, 496, 500-501.
- Pence, James W. 1967. Factors affecting bread flavor. Bakers Digest 41(2):34-36, 85.

Color, Texture and Other Quality Factors

- Bagni, N., Caldarers, C. M., and Moruzzi, G. 1967. Spermine and spermidine distribution during wheat growth. Experientia 23:139-41. 1/
- 1/ Research supported by P.L. 480 funds.

- Bernardin, J. E., Kasarda, D. D., and Mecham, D. K. 1967. Preparation and characterization of alpha-gliadin. *J. Biol. Chem.* 242(3):445-50.
- Elton, G. A. H. and Fisher, N. 1966. A technique for the study of the baking process, and its application to the effect of fat on baking dough. *J. Sci. Food Agr.* 17(6):250-4. 1/
- Escribano, M. J., Keilova, H., and Grabar, P. 1966. Study of gliadin and glutenin after reduction or oxidation. *Biochim. Biophys. Acta* 127(1): 94-100. 1/
- Fisher, N., Bell, Brenda M., Rawlings, Christine E. B., and Bennett, Ruth. 1966. The lipids of wheat. III. Further studies of the lipids of flours from single wheat varieties of widely varying baking quality. *J. Sci. Food Agr.* 17(8):370-82. 1/
- Fullington, J. G. and Hendrickson, H. Stewart. 1966. Phospholipid-metal complexes. Interaction of triphosphoinositide- and phosphatidylserine-metal complexes with ethylenediamine, polyamino acids and protein. *J. Biol. Chem.* 241(17):4098-100.
- Hibberd, G. E. and Wallace, W. J. 1966. Dynamic viscoelastic behaviour of wheat flour doughs. Part I: Linear aspects. *Rheologica Acta* 5(3): 193-198. 1/
- Hrazdina, Geza. 1967. Concerning isolation and characterization of a xylanase from a commercial cellulase preparation. Ph.D. Dissertation, Eidgenossische Technische Hochschule, Zurich, Switzerland. 1/
- Hui, P. A. 1966. Recent investigations on wheat pentosans. *Getreide und Mehl* 16:73-6. 1/
- Kasarda, Donald D., Bernardin, John E., and Thomas, Richard S. 1967. Reversible aggregation of alpha-gliadin to fibrils. *Science* 155(3759): 203-05.
- Mamaril, F. P. and Pomeranz, Y. 1966. Isolation and characterization of wheat flour proteins. IV. Effects on wheat flour proteins of dough mixing and of oxidizing agents. *J. Sci. Food Agr.* 17(8):339-43. (Contract)
- Pace, J. and Stewart, B. A. 1966. Dough development in relation to disulphide and thiol groups. *Milling* 146(13):317-8. 1/
- Pomeranz, Y., Chung, Okkyung, and Robinson, R. J. 1966. Lipids in wheat from various classes and varieties. *J. Amer. Oil Chem. Soc.* 43(8): 511-14. (Contract)

Stevens, D. J. 1966. The reaction of wheat proteins with sulphite, II, The accessibility of disulphide and thiol groups in flour. J. Sci. Food Agr. 17(5):202-4. 1/

Tanaka, Kenji, Furukawa, Kazuyo, and Matsumoto, Hiroshi. 1967. The effects of organic and inorganic acids on the physical properties of dough. J. Ferment. Technol. 45(6):566-569. 1/

Microbiology and Toxicology

Wiseblatt, Lazare. 1967. Reduction of the microbial population in flours incorporated into refrigerated foods. Cereal Chem. 44(3):269-80. (Contract)

Technology--Process and Product Development

Barta, E. J., Kilpatrick, P. W., and Morgan, A. I., Jr. 1966. Methods of peeling wheat. U.S. Patent No. 3,264,113.

Bloch, Felix and Morgan, Arthur I., Jr. 1967. Germination inhibition in wheat and barley during steeping, and alpha-amylase development in the presence of gibberellic acid. Cereal Chem. 44(1):61-9.

Copley, M. J., Ferrel, R. E., and Pence, J. W. 1966. Processing of wheat and product produced therefrom. U.S. Patent No. 3,228,771.

Fellers, David A., Shepherd, Allan D., Bellard, Nancy J., and Mossman, Albert P. 1966. Protein concentrates by dry milling of wheat millfeeds. Cereal Chem. 43(6):715-25.

Fellers, David A., Shepherd, Allan D., and Pence, James W. 1966. From wheat byproducts low cost protein for new products. Food Processing/Marketing 27(10):98-9.

Ferrel, R. E., Shepherd, A. D., Thielking, R. H., and Pence, J. W. 1966. Gun-puffing wheat and bulgur. Cereal Chem. 43(5):529-37.

Morgan, A. I., Jr., Barta, E. J. and Graham, R. P. 1966. Chemical peeling of grain. Chemical Engineering Progress Symposium Series 62(69):138-41.

1/ Research supported by P.L. 480 funds.

AREA NO. 2. WHEAT UTILIZATION - FEED

Problem. Wheat can now compete with feed grains as animal feed because recent legislation on wheat pricing makes it economically feasible. In the last two years the use of wheat for feed increased to over 100 million bushels per year, more than twice the amount used in other recent years. Projected usage for 1967 again is slightly higher. Unfortunately, wheat, especially Western wheats, has certain performance drawbacks particularly as a feed for poultry. Research to improve the feeding quality of wheat would greatly benefit both growers and feeders in wheat-producing areas, since it would place this grain in a better competitive position with other grains.

Millfeeds are not used extensively in modern poultry and swine rations because the high fiber content cannot be tolerated in high-energy rations. Ways to separate low-fiber, high-protein fractions from millfeeds have been developed. If these new materials can be produced cheaply enough, they can be used as protein and energy sources for non-ruminant diets, and the overall value of milling byproducts will be increased. An alternative approach is to increase the digestibility of millfeeds by process treatments much as steam pelleting or enzymatic supplementation or digestion. Flour production is expected to increase in the near future to reflect the demands of our increasing domestic population and of the new export markets which are developing. More milling will result, of course, in more millfeeds. If these millfeeds can be utilized efficiently and effectively, the price for flour will not have to increase to carry the economic burden imposed by the expansion of milling facilities.

Meat production, particularly poultry, is increasing rapidly in Japan and the European Economic Community where modern efficient methods have been introduced. This development depresses the opportunity for exporting poultry and other meats into these important trade areas, but it offers an increasing opportunity to sell feeds. Upgrading of wheat millfeeds through utilization research will increase our export markets.

USDA AND COOPERATIVE PROGRAM

Research at Albany, California, on utilization of wheat seeks to develop new processes to convert milling byproducts into higher value feeds and to modify whole wheat so that it is more economical for use as a feed grain. Research on barley is also conducted.

The Federal program of research in this area totals 1.9 scientist man-years. Research is conducted on technology--process and product development.

PROGRAM OF STATE EXPERIMENT STATIONS

A total of 0.6 scientist man-years is devoted to this area of research.

PROGRESS -- USDA AND COOPERATIVE PROGRAMS

A. Technology--Process and Product Development

1. Enhancing Nutritive Value and Biological Activity of Cereal Fractions for Animal Feeds. We are conducting studies to develop processing treatments for wheat and barley fractions which will improve the nutritive value and biological activity of these fractions for animal feeds. Since samples of bran mash before and after pelleting show only slightly different chemical composition but significantly different metabolizable energy values, we are trying to establish which component has changed enough to upgrade the pelleted material. In vitro tests with popped wheat and barley indicate increased digestibility of processed material. By building a 1/2 ton per hour cereal popping machine, we can now process enough grain for animal feeding tests. Popped, rolled grains show promise in making high-molasses rations easier to handle.

The lipid and fatty acid contents of seven representative wheats and their derived millfeeds were determined. Also, several Pacific Northwest wheats and millfeeds were analyzed to relate nutritional variability to composition.

AREA NO. 3. RICE UTILIZATION - FOOD

Problem. Limitations on U.S. rice acreage are being relaxed because of the increasing need for rice to export into food-short areas, particularly Southeast Asia. Polished rice is a relatively expensive source of nutrients because its protein, although high in quality, is only about 5% to 7% of the kernel, and it is almost devoid of vitamins. The need is for new and improved food products with better nutritive quality and produced at minimum increase in cost. Such products must be easy to prepare; have good texture, flavor, and appearance; and be economical to manufacture. Also needed are drastically improved milling methods to increase economic returns to growers and millers so that cost to consumers will not increase. Detailed knowledge of chemical composition and physical properties as related to processing is needed to guide the developments in milling, processing, and development of products that meet the growing export demand.

USDA AND COOPERATIVE PROGRAM

In the Western Utilization Research and Development Division, basic and applied research is conducted at Albany, California, and, by contract at Berkeley, California, on rice proteins, debranning of brown rice by lye-peeling, parboiling of brown and under-milled rice, new methods to produce quick-cooking forms having better flavor and texture, and conversion of high-protein flours into beverage products especially suitable for infant feeding overseas.

The Federal program of research in this area totals 2.3 professional man-years, assigned to investigations of technology--process and product development. In addition, the Division sponsors one research grant under P.L. 480 in Japan.

PROGRAM OF STATE EXPERIMENT STATIONS

A total of 0.8 scientist man-years is devoted to this area of research.

PROGRESS -- USDA AND COOPERATIVE PROGRAMS

A. Technology--Process and Product Development

1. Development of New Rice Products Such as Deep Milled Rice Flour, Improved Quick-Cooking Rice and Rice of Improved Flavor Stability. We are conducting research designed to improve the color, flavor, and convenience of conventional consumer rice products. Also, we are seeking to develop new high-protein products for growing specialty markets. To do this we are studying rice proteins, particularly in relation to processing procedures or cooking properties. Determinations were made of the distribution of

proteins in typical varieties of milled rice. We found the proportions of albumin (water-soluble proteins) and globulin (proteins which are soluble in a salt solution) increased markedly from the inner to outer rice kernel. Prolamin (protein soluble in 60-80% alcohol) is evenly distributed throughout the kernel and the proportion of Glutelin (protein soluble in dilute acids and alkalis) increases toward the center. The albumins in milled rice have strong amylase activity; the globulins have little. We have analyzed a purified single globulin component, molecular weight 25,500, and found it contained no lysine, histidine, or amylase activity. An analysis of rice bran indicates that the albumins and globulins in the bran differ from those in milled rice.

Infusion with lysine solution raised the lysine level in milled rice to nearly 6%. Addition of soy flour to rice at this lysine level caused color and flavor differences.

Control methods developed at the Western Utilization Research and Development Division are increasing rice drying rates in columnar dryers by 35-40% without additional breakage during subsequent milling.

Contract research has been initiated at the University of California in Berkeley to evaluate the cooking and processing characteristics, utility of new products, and optimum economic balance of products from white rice overmilled to various degrees.

Milk-like products were made with limited success from high protein rice flours using an amylase-pepsin process developed for wheat. Other enzymes tested for their solubilizing effect on the rice proteins were not as effective as pepsin, although three showed promise as acceptable protein-dispersing agents.

PUBLICATIONS -- USDA AND COOPERATIVE PROGRAMS

Technology -- Process and Product Development

Houston, David F. and Mohammad, Ali. 1966. Air classification and sieving of rice bran and polish. The Rice J. 69(8):20-1.

Houston, David F., Morgan, A. I., Jr., and Pence, J. W. 1966. Rice investigation at Western Regional Research Laboratory. The Rice J. 69(7):82-5.

Houston, D. F. 1967. Recent U.S. Developments in Rice Husk Utilization. In "Rice Byproduct Utilization," Food and Agr. Organization of the U.S. Informal Working Bulletin 30, pp. 13-16.

Houston, David F. 1967. Utilization of Rice Husks. In "Rice Byproduct Utilization," Food and Agr. Organization of the U.S. Informal Working Bulletin 30, pp. 7-11.

Potter, Earl F. and Long, Marion C. 1966. Colorimetric determination of calcium in rice and wheat. J. Assoc. Off. Analyt. Chem. 49(5):905-6,

AREA NO. 4. FORAGE UTILIZATION - FEED

Problem. The demand for livestock in the United States will increase 45% by 1975. Since forage crops constitute the major feedstuff for ruminant animals, the demand for forages will increase accordingly. In addition, there is an increasing demand for processed forages in European and Asiatic markets as well as in domestic markets. Fresh forage crops are the richest natural source of many nutrients for farm animals. Forages, however, are preserved so inefficiently by hay-making and ensiling that 10 to 50% of the dry weight and much larger fractions of the most valuable nutrients are lost before the animals eat them. Dehydration is now the only practical means of producing products of high nutritional value in a form usable in manufactured feeds and supplements. Poultry and swine producers are aware of the value of dehydrated forage, but restrict their use of it because of its high fiber and growth-inhibitor content. There is evidence that certain unidentified growth factors are lost, at least partially, during the dehydration process as presently carried out. The livestock breeder needs forage products tailored to specific animals, and the forage producer must adapt to his needs to sell.

Basic and applied utilization research are necessary to produce: (1) high-protein, low-fiber feeds rich in unidentified growth factors designed for use by non-ruminant animals; (2) fiber products which have been cheaply treated to make them easily digestible for ruminants; (3) growth-stimulating supplements for ruminants, derived from the biologically active fiber-digestion factors and growth-promoting factors in forage. New products should be adaptable to mechanical feeding. Improved uses will encourage farmers to put high-value land into forage crops.

USDA AND COOPERATIVE PROGRAMS

Current research in the Western Utilization Research and Development Division includes both basic and applied studies on all forages used or potentially usable for off-the-farm processing. The research is conducted at the Division headquarters at Albany, California; under contracts at Lincoln, Nebraska, and Tifton, Georgia; and under P.L. 480 grant programs in Israel and Italy. The mechanical separation of leaf from stem of alfalfa is being studied with financial support from the Department of Agriculture and Inspection of the State of Nebraska and the cooperation of several experiment stations and commercial processors and users of forages. Products are being evaluated at the University of Nebraska, Kansas State University, Purdue University and the Agricultural and Mechanical College of Texas. Research on increasing the digestibility of stem carbohydrates by ruminants is being done under contract at the University of Nebraska. Also under study are biologically active forage constituents (such as the guinea pig and chick-growth-promoting factors in forages and alfalfa saponins which depress chick growth), organic acids of alfalfa, non-

protein nitrogen compounds of alfalfa, and the mechanism of action of forage antioxidants. The guinea pig growth factor work is being done in cooperation with the University of California in Berkeley. Processing of forages by "wet" (juicing) methods is being investigated in cooperation with a commercial company. The effects of dehydration conditions on losses of carotene and xanthophyll are being studied.

The Federal program of research in this area totals 6.7 scientist man-years, including one scientist whose salary is provided by the Department of Agriculture and Inspection, State of Nebraska, and contract research. Research is conducted on technology--process and product development. In addition the Division sponsors, under P.L. 480, three research projects on forages.

PROGRAM OF STATE EXPERIMENT STATIONS

A total of 4.2 scientist man-years is devoted to this area of research.

PROGRESS -- USDA AND COOPERATIVE PROGRAMS

A. Technology--Process and Product Development

1. Improved Feeds from Alfalfa and Other Forage Crops. Lipids are major contributors to the biological value of alfalfa, but they are subject to oxidative deterioration. An investigation of certain lipid constituents of alfalfa and their relationship to the autoxidation of alfalfa carotenoids has been concluded at the University of California in Berkeley. This study showed that during the first 24-hour holding period after harvesting, freshly cut alfalfa lost approximately 75% of the beta-carotene contents, 12% of the extractable lipids, 30% of the linolenic acid, and 60-75% of the galactolipids, and the free fatty acid content doubled. The holding period also decreased somewhat the effectiveness of ethoxyquin in protecting the lipid constituents. During a second 24-hour holding period the extractable lipids showed another sharp decrease. The losses of other lipid constituents were considerably smaller than those found during the first 24-hour period. These data re-emphasize the importance of keeping the time between harvest and dehydration at an absolute minimum.

Analytical procedures were developed to determine the amounts of galactolipids, beta-carotene, total extractable lipid and fatty acids in fresh lyophilized alfalfa. These methods were used in determining the lipid changes which occur in freshly cut alfalfa before and after dehydration and in stored dehydrated meal with and without added ethoxyquin. Monogalactolipid was 11-14% of the total lipids and digalactolipid was 6-7%. Unlike phosphatidyl choline and phosphatidyl ethanolamine these purified complex lipids showed no synergistic antioxidant activity in squalene or menhaden oil. Digalactolipid showed some prooxidant activity. The length of time the alfalfa was held prior to lyophilization did not grossly alter the effectiveness of ethoxyquin in protecting the lipid constituents in the dehydrated meal.

Because of their association with biological activity, phenolic compounds of alfalfa and other forages are under investigation. Characterization work has been completed on a number of previously isolated phenolic compounds. They include the novel dicoumarin, daphnoretin, from ladino clover, as well as two flavones previously unreported in nature, 7,4'-dihydroxyflavone and 7,3',4'-trihydroxyflavone. Alfalfa has been shown to contain a whole family of coumestans of which coumestrol may be considered to be the simplest member. To date, a total of eight such coumestans have been characterized. They include coumestrol, 3'-methoxycoumestrol, 4'-methoxycoumestrol, lucernol, medicagol, sativol, trifoliol, and 7-hydroxy-11,12-dimethoxycoumestan.

Studies conducted in cooperation with the Alfalfa Investigations of the Crops Research Division of the Agricultural Research Service to show the relationship of disease to buildup of phenolic compounds in forages have been completed. They demonstrated that plant diseases such as common leaf spot and rust will produce a very rapid "buildup" of a number of phenolic compounds in the forage plant. The total amount of each compound appears to increase with the severity of the attack. The compounds predominate around the locus of the infection, suggesting that the compounds may in some way be related to the protective or disease-resistance mechanism of the plant. In related work, in cooperation with Purdue University it has been found that the levels of coumestrol and other phenolics may also be under genetic control.

A limited number of tests of the anti-fungal properties of coumestans were carried out. Under the test conditions employed, no anti-fungal activity was observed. Limited tests were also carried out for insecticidal properties in cooperation with the Entomology Division of the Agricultural Research Service at Beltsville also with negative results.

Studies relating to the growth-promoting effects of coumestrol on large animals have continued in cooperation with Purdue University and American Dehydrators Association. The most recent work, in which pure crystalline coumestrol has been fed in the diet of beef cattle has not confirmed the growth responses previously obtained with cruder extracts. This suggests that other presently unidentified factors present in the crude extracts may have been the actual growth-promoting agents.

Contract research is being conducted at the University of Georgia to improve processed forages by determining the effects of unit industrial processes on the chemical composition and nutrient availability of dehydrated forage crops. Gahi millet and Coastal Bermuda grass were grown with varying fertilizer combinations with and without irrigation. Serial cuttings of the Coastal Bermuda were made at 3-1/2 week intervals. Three cuttings of millet were made in July, August and September. Analytical and stability studies are not complete. Xanthophyll utilization tests show that dehydrated millet is significantly better than Coastal Bermuda grass in promoting xanthophyll deposition in chicks. Other comparisons

showed the millet's deposition of xanthophyll was at least equal to that of alfalfa, and both were superior to corn gluten meal which ranked close to the Coastal Bermuda grass.

Contract research is being conducted at the University of Nebraska in Lincoln to increase the use of alfalfa in mixed feeds by removing or degrading lignin and thus increasing the availability of the cellulose to ruminants. A variety of treatments were evaluated for their effects on the digestibility of alfalfa stem materials. Incubation with acids had no effect but incubation with a number of basic or peroxidic compounds increased digestibility significantly, as determined by artificial rumen studies. Water content, temperature, and heating time were not critical. Digestibility increases of up to 33% were achieved with ethanolamine-water mixtures. Treatments with sodium or hydrogen peroxide gave inconsistent results. Other reagents used in the wood industry were found to be inferior to the above treatments. Removal of water-soluble constituents of the stem prior to treatment had no effect, nor was excess oxygen helpful. In a sheep experiment, rumen microorganisms made inefficient use of ethanolamine, and in vivo results correlated with "artificial rumen" tests. The results indicate that it is not necessary to completely destroy lignin in order to markedly improve cellulose digestion.

We are conducting research to develop rapid microbiological or other assay procedures that correlate with guinea pig and chick growth response to alfalfa. Microbial assay of alfalfa juice concentrate for unidentified growth factors was begun. Activity could be chromatographed into three fractions: the material not absorbed on the column, material eluted from the column with 10% ammonium hydroxide, and material eluted with hydrochloric acid. Each fraction was inactive, but by recombining the materials eluted with hydrochloric acid and ammonium hydroxide, most of the activity of the original alfalfa was accounted for. About 80% of the material eluted with hydrochloric acid was attributable to magnesium. Essentially all of the remaining activity was attributable to calcium and potassium salts. Isolation studies on the material eluted with ammonium hydroxide are now underway.

Addition of 10% dehydrated alfalfa to the diet of guinea pigs resulted in improvement in growth of up to 50 grams over a 3-week assay period. The unidentified factor(s) appears to be distinct from all known vitamins, minerals, amino acids, or other nutrients, and it appears to be organic in nature, since it is not found in the ash of alfalfa. This work is being done in cooperation with the University of California in Berkeley.

P.L. 480 funds are supporting two research projects in Israel. The Hebrew University-Hadassah Medical School in Jerusalem has begun a study to isolate and evaluate anti-estrogen components from alfalfa to guide the development of improved dehydration procedures. Research to detoxify or remove growth-depressing saponins from alfalfa feeds is being conducted at the Hebrew University in Rehovot.

The Experiment Station for Practical Agriculture in Milano, Italy, supported by P.L. 480 funds is investigating the factors effecting the variability of natural antioxidant in alfalfa to improve stabilization of dehydrated products. Chromatography of pigment-free lipid extracts produces seven fractions with reducing activity. These substances increase rapidly during the first vegetative phases. One principal component has been tentatively identified as plastohydroquinone. Activity is present in leaves but not in the stem. Several components are destroyed by dehydration; one, however, is markedly increased and remains stable for 200 days storage. A rapid preparative technique for isolation of individual components has been developed.

We are studying processing techniques which might develop forage feeds with enhanced biological activity. We have found that up to 70% of the xanthophyll in alfalfa was lost during dehydration. Losses correlated with the dehydrator outlet temperature and the moisture of the meal. Of the xanthophylls, lutein was more stable than neoxanthin or violaxanthin. A new analytical procedure for xanthophyll of alfalfa permits prediction of pigmentation of broilers and correlates with corn gluten xanthophyll analysis. Neoxanthin was detected in broiler skin. Research on non-protein nitrogen compounds of alfalfa showed that the quantity of stachydrine in alfalfa greatly exceeds that of betaine. An unknown related compound is also present. We analyzed eight alfalfa samples and their fiber residues for protein, fat, fiber, ash, pentosans, lignin, anhydrouronic acid, starch and reducing sugar. Air classification of leaf-stem was conducted in a zig-zag type separator on full production scale. Stem meal was found to be pelletable if proper conditions were used.

2. Improved Stability of Alfalfa and Other Forage Products for Export. We are conducting research to develop practical techniques for processing forages to stabilize or concentrate the valuable components of forages. The use of alfalfa in mixed feeds for poultry is based principally on its xanthophyll content. We have found that up to 70% of the xanthophyll in alfalfa can be lost during dehydration. These losses correlated with the dehydrator outlet temperature and the moisture of the meal.

PUBLICATIONS -- USDA AND COOPERATIVE PROGRAMS

Technology--Process and Product Development

- Aspinall, G. O. and McGrath, D. 1966. The hemicelluloses of lucerne, J. Chem. Soc. (C):2133-2139. 1/
- Bickoff, E. M., Spencer, R. R., Knuckles, B. E., and Lundin, R. E. 1966. An alfalfa coumestan. 3'-methoxy-coumestrol from alfalfa: isolation and characterization. J. Agr. Food Chem. 14(5):444-6.
- Bickoff, E. M., Loper, G. M., Hanson, C. H., Graham, J. H., Witt, S. C., and Spencer, R. R. 1967. Effect of common leafspot on coumestans and flavones in alfalfa. Crop Sci. 7:259-261.
- Hutson, D. H. 1967. 6-S- β -D-Glucopyranosyl-6-thio-D-glucopyranose. A. Thioglycosidic analogue of gentiobiose. J. Chem. Soc. (C):442-444. 1/
- Kohler, G. O., Knowles, R. E., and Livingston, A. L. 1967. An improved analytical procedure for the determination of xanthophyll. J. Assoc. Off. Analyt. Chem. 50:707-11.
- Livingston, A. L., Knowles, R. E., Israelsen, M., Nelson, J. W., Mottola, A. C., and Kohler, G. O. 1966. Processing changes. Xanthophyll and carotene stability during alfalfa dehydration. J. Agr. Food Chem. 14(6): 643-4.
- Nelson, J. W., Livingston, A. L. 1967. Stabilization of xanthophyll and carotene by ethoxyquin during thin-layer chromatography. J. Chromatog., 28:465-67.
- Polesello, A. and Vistarini, S. 1965. Separation on TLC and determination of alpha-tocopherol and beta-carotene in forage plants. Journees Hellenes de Separation Immediate et de Chromatographie, pp. 101-6. 1/
- Polesello, A. and Vistarini, S. 1966. Distribution and evolution of lipid antioxidants of alfalfa leaves. Proc. Vith International Symposium of Agrochemistry, Varenna, Italy. 1/
- Spencer, R. R., Knuckles, B. E., and Bickoff, E. M. 1966. Synthesis of a series of isomers of coumestrol. J. Heterocyclic Chem. 3:450-3.
- Spencer, R. R., Witt, S. C., Lundin, R. E., and Bickoff, E. M. 1967. Bicoumol, a new bicoumarinyl, from ladino clover. J. Agr. Food Chem. 15(3):536-38.

1/ Research supported by P.L. 480 funds.

Stuthman, D. D., Bickoff, E. M., Davis, R. L., and Stob, Martin. 1966.
Coumestrol differences in Medicago sativa L., free of foliar disease
symptoms. Crop Sci. 6(4):333-4.

AREA NO. 5. WOOL AND MOHAIR UTILIZATION

Problem. Traditional markets for wool and mohair have been lost to synthetic fibers because consumers prefer garments that hold their pleats and creases, resist shrinkage and wrinkling during washing, and dry quickly. Natural wool and mohair outclass the synthetics in tailorability, comfort in wear, appearance, and hand, but lack certain features now being exploited by the promoters of synthetics. Furthermore, some current processing methods damage, distort, or weaken wool and mohair fibers and injure performance and appearance of the fabric. We need processes that will modify natural fibers to give a range of comfortable and attractive fabrics that resist deterioration in processing and wear. Fabrics must be durably resistant to wear, wrinkling, pilling, abrasion, yellowing, soiling, felting and relaxation shrinkage, acid and alkali weakening, insects, and micro-organisms. New markets in industrial and other uses would develop for new types of fabrics, woven and non-woven, made from natural wools and from blends of wool with modified wools or other fibers. Wool could have a part of the new, developing market for stretch fabrics if we could practicably impart permanent stretch into wool yarn. Research toward such developments requires fundamental information on the chemical, physical, and structural nature of natural fibers and their modified products.

To sustain a stable sheep and wool industry in the United States, mills must be supplied with processing information on new and improved wool and mohair products. Synthetics have cut into wool markets because the synthetics are uniform in price and quality and because detailed processing information is available from producers.

USDA AND COOPERATIVE PROGRAM

The Western Utilization Research and Development Division conducts a broad basic and applied research program on wool and mohair to develop new and improved fibers and fabrics that can increase markets. Fundamental research seeks new facts on chemical and physical properties of natural fibers, and we use such knowledge to modify fibers and fabrics so that they will resist degradation by heat, light, chemicals, staining, abrasion, and insects; retain creases; shed wrinkles; and require little care. Department scientists bring research results to the industry through technical publications, public service patents, exhibits, news media and conferences.

The Federal program is conducted at the Division headquarters at Albany, California; by contract in Durham, North Carolina, and Washington, D. C.; and by grant funds under P.L. 480 in India and Sweden.

The Federal program of research in this area totals 26.4 scientist man-years, including contract research. Of this number, 19.4 are assigned to

chemical and physical investigations to improve products and 7.0 to technology--process and product developments. In addition, the Division sponsors six research grants under Public Law 480.

PROGRAM OF STATE EXPERIMENT STATIONS

A total of 0.9 scientist man-years is devoted to this area of research.

PROGRESS -- USDA AND COOPERATIVE PROGRAMS

A. Chemical and Physical Investigations to Improve Products

1. Improved Ease-of-care Properties Through Fiber Modification. We are conducting research to provide basic information on the mechanical and physical properties of fibers, fiber assemblages, and fabrics and to determine the effects on these properties of treatments developed to improve fabric performance. We have found that appraisal of wool-cellulosic blend fabrics and garments treated for wash-wear performance requires wear tests in addition to laboratory testing. Felting shrinkage is completely controllable with interfacial polymerization (WURLAN I) and phase-boundary-limited crosslinking (WURLAN II) treatments. We are testing a new device for the appraisal of fuzz on fabrics. Physical property and wash performance data for many control and treated fabrics await correlation with wear trials. An interlaboratory test of an improvement in strength testing of wool fiber bundles was conducted for the American Society for Testing and Materials and Method 2524 was revised to include the use of a standardizing wool. Also, we have improved the technique for testing wool yarn abrasion.

The application of high-energy radiation to initiate grafting of polymers onto wool fibers is being studied under contract at the Research Triangle Institute, Durham, North Carolina. Rates of grafting and molecular weights of the polymer side chains grafted in situ have been determined for mutual and pre-irradiation grafting systems. Formic acid enormously increases the yields of grafting in wool. Pre-irradiation grafts have much shorter chain lengths than the corresponding mutual products. Measurements have revealed that, with pre-irradiation grafting, the free radical population levels off at a lower value with lower dose rates, and as expected, the population contains much more of the more stable radical species at the lower dose rates. Electron microscopy and small-angle X-ray scattering have helped to locate the grafted polymer in cell walls and inside the cell structures.

Stress-strain measurements on wool fibers modified by different polymers show that only minor changes in properties result from in situ grafting of as much as 20% of the polymers.

In order to predict and interpret the value of natural and modified fibers, we are studying the relationships of structure, composition and properties. We have written computer programs to process data on the amino acid composition

of wool proteins and peptides and also to calculate molecular weight distribution from ultracentrifugal sedimentation data. Wool is half soluble in aqueous reducing media at pH 2.6. The soluble part has a molecular weight mostly over 10,000 and when sedimented free from salts forms a gel which has an ultrastructure of uniform rods resembling wool microfibrils.

Structure development in wool is best explained by electrostatic stabilization from alternating isoelectric-point regions. Electrostatic forces can also greatly affect the kinetics of diffusion-controlled aggregation. Changes in mechanical properties accompanying wool swelling are anisotropic. Direct observation of swelling anisotropy in various parts of wool fibers is in progress. We are conducting research to develop continuous processes to bleach, improve dyeing properties and tensile strength, and produce durable shrink resistance in wool top, yarn and fabric. A wool-top drafting attachment has been incorporated in the corona discharge equipment to provide a thin webbing of wool fibers for continuous treatment in the corona reactor. Electrostatic fiber attraction to the electrodes is avoided by a conveyor belt made of Teflon-covered rods at appropriate spacing. Temperature is thermostatically controlled. Optimum temperature for treatment is 92-105° C. Chlorine gas in the electrical discharge regions markedly promotes the shrink-resist reaction. It is mixed with air and injected through holes in one electrode. Reactivity increases with the frequency of the corona electric field. Pretreatment of wool with dilute solutions of some metal salts, followed by drying, improves shrink resistance. With control of moisture content, electrical voltage, and accelerators, highly promising results were obtained.

We studied the effect of radiant energy upon wool fibers, with particular emphasis upon those parts of the spectrum to which wool is normally subjected. Among our important findings was a photophysical phenomenon which we called "Spectral Conformity." This appears to be a newly-recognized process by which a molecule dissipates absorbed radiant energy-without undergoing major chemical change. A curious consequence of this effect is that wool and many other materials--rubber, plastics, paper, cotton, silk, nylon, etc., become permanently bluer in blue light, for example. Our studies showed that yellowing of wool occurs in the ultraviolet region, whereas bleaching occurs in the visible spectrum, and the net effect will depend upon the spectral distribution of the radiating source, electrical or sunlight. The net effect of sunlight depends upon time of day, season, latitude, altitude, and atmospheric transmission, and thus varies with place and time. Of particular interest was the spectral transition region, in which yellowing and bleaching are caused simultaneously by a given wavelength, about 365 mμ. Of considerable theoretical interest was the greening of wool at 254 mμ. This was shown to be due to the simultaneous production of two independent absorbers, one absorbing blue light and the other, orange light.

Supported by P.L. 480 funds, the University of Allahabad in India is studying the interactions of organic molecules within wool fibers, In glycerol-water

solutions, sound absorption is maximum at 14 mole-percent observed at a frequency of 0.5 megacycles/second, and at 50 mole-percent at 0.8 megacycles/second. These results indicate that complexes form between water and glycerol, and suggest a possible new approach to the study of interactions in solution complexes with mole ratios of 1:6 and 1:1 (glycerol:water).

The Ahmedabad Textile Industries Research Association in India, supported by P.L. 480 funds is making measurements of the adsorption energy of selected ions to wool in order to determine the accessibility of ion exchange sites as loci for chemical modification. Analytic techniques for determining sodium, chloride and phosphate ions have been adapted to the determination of these ions adsorbed to wool and used to investigate extent of the adsorption of such ions to natural wool from 0.05 molar solutions of sodium chloride and trisodium phosphase at 50° C. The results are in accordance with non-specific binding to the wool protein which acts as an ion exchanger.

P.L. 480 funds are supporting a third research project in India. The Indian Institute of Technology in Kanpur, India, has begun a study to explain the mechanical behavior and structure of fibers as a function of molecular configuration.

The German Wool Research Institute in Aachen, West Germany, is supported by P.L. 480 funds to correlate chemical and physical properties of fine, coarse, and chemically modified wools with X-ray diffraction measurements. Specific staining of lysine in wool fibers is possible. Low-angle X-ray diffraction showed an axial periodicity of 39 Å for lysine residues in the structural units of mohair, and a distribution of these residues on the periphery of protofibrils. Results with Lincoln wool were similar. In contrast to earlier interpretations, evidence was found for microfibrillar swelling in alpha keratin fibers. The helices of the matrix are ordered in fiber direction, and their lateral spacings do not increase during swelling in water. Inter-microfibrillar spacing varies with the type of fiber. A quantitative correlation between crystallinity and mechanical properties was demonstrated with different types of alpaca.

Research to determine the sulfur distribution within wool keratin and its relation to the dimensions and aggregation of fibrillar components is being conducted at the Karolinska Institutet in Stockholm, Sweden, supported by P.L. 480 funds.

2. Improved Ease-of-care Properties Through New Finishing Treatments.

To improve wool's competitive position with easy-care synthetics, we are screening potential treatments for making wool fabrics resistant to shrinking, soiling, wrinkling, pilling, yellowing, and abrasion. Cross-linking wool in fabric form by reaction with sebacyl chloride, one of the WURLAN reactants, did not result in durable press performance; wrinkling was worse after machine washing and tumble drying. A study was also made

of crosslinking reactions initiated in wool protein in solution with peroxydisulfate. Steric effects influence the reaction rate of persulfate with model peptides. The main attack is on the peptide alpha-carbon. Riboflavin-sensitized photopolymerizations of acrylic monomers proceed in the presence of proteins, amino acids, or peptides; the reaction depends on concentration and chemical nature of both monomer and protein. Wool treated with epoxides and then given the dihydroxy-dimethylolethyleneurea (DHDMEU) treatment, effective for durable press in cotton, showed only slight crease retention. DHDMEU caused wool to yellow on heating and reduced its abrasion resistance but did not reduce the fabric breaking strength or affect supercontraction. Novel dyeing of wool was achieved by coupling diazonium salts with wool. Also, with conventional dyes, a higher rate and better levelness of dyeing were obtained in wool pretreated with ethanolamine sulfite. New water and oil-repellent finishes derived from copolymerization of fluoroalkyl silanes and alkyl halosilanes are highly effective. Several new compounds were synthesized.

Contract research is being conducted by Harris Research Laboratories, Washington, D.C., to obtain basic data on low-cost protective finishes for wool and mohair. Polymers of 1, 1-dihydroperfluorooctyl acrylate (PFOA) and 1-(perfluorooctanoyl) aziridine (PFOAz) were prepared. The critical surface tension of wetting (CST) of PFOA was 10.3 dynes/cm. CST of PFOAz on wool fibers was less than 16 dynes/cm. Solutions of PFOA were prepared with five non-fluorinated extenders: poly(vinyl stearate), poly(stearyl acrylate), polyethylene, a polyamide, and a polyurethane. The critical surface tensions of wetting of PFOA-poly(vinyl stearate) mixtures were determined both by contact angle measurements and by observing whether coated fine glass rods float or sink on each member of a series of alkanes. By the contact angle method, 4% PFOA in poly(vinyl stearate) produced a CST of 15.7 dynes/cm., 7 dynes/cm. less than that of poly(vinyl stearate). By the coated rod technique, much less PFOA was needed to obtain a similar reduction in CST. This difference may be related to phase separation of the two polymers as the solvents evaporate. Since a very small amount of fluoropolymer can be extended with a great amount of relatively low-cost non-fluorinated material to produce a protective finish with low critical surface energy, highly effective, low-cost protective finishes for fabrics may be possible.

We are conducting research to improve and expand the use of interfacial polymerization (WURLAN I) and phase-boundary-limited crosslinking (WURLAN II) for wool textile finishing. The WURLAN I process for shrink-resist treatment of wool fabric has been improved by using an aromatic petroleum solvent. Advantages include better shrinkproofing, handle, reactant stability, and dyeability, lower cost, and simpler process control. Wool top has been treated effectively without using a strong alkali, and results are promising for blanket and wool knit material.

Studies of WURLAN II have focused on interfacial application of low-cost reactive isocyanate prepolymers. Although hand and wool stabilization

are excellent, reactant stability is unacceptable. Alternative reactants are being studied.

Contract research to determine the effect of selected chemical treatments on the luster of wool fabrics has been concluded. In connection with measurement of luster of wool fibers and fabrics, the investigators, Harris Research Laboratories, Inc., Washington, D.C., examined the properties of the wool fiber itself to determine the factors which influence the reflection or scattering of light from wool. The most significant factors were crimp and scale structure. For the precise measurement of luster, a method was developed for accurately measuring light reflected from wool, either single fibers or fabrics.

Methods for increasing the luster of wool fabrics were compared. Where luster arises from oriented pile fibers, as in velour coating fabrics, the luster can be increased and made more durable by light interfacial polymerization treatments, or by reduction and setting by monoethanolamine sulphite. When luster depends on the surface properties of the fibers, as in clear finish worsteds, some of the oxidative or subtractive antifelting treatments also add to luster. Chlorination by gas, or acid hypochlorite treatments, are the most favorable. Adverse effects on hand limit these treatments. Other oxidative shrink proofing treatments show less improvement in luster, or even lower it.

The Institute for Fibres and Forest Products Research in Jerusalem, Israel, supported by P.L. 480 funds, is conducting research to relate fiber crimp to chemical, physical, and mechanical properties of wool and determine the effects of processing on crimp. A method for defining and measuring crimp was applied to wool fibers. A computer program was developed to provide statistical evaluations and correlations between crimp parameters and mechanical properties of wool. Three types of wool were measured and crimp parameters obtained for a series of loadings on each fiber. The three wool types can be graded according to their crimp diameters, wave numbers, and uncrimping energies. Effects of water on dynamic crimp parameters and on Young's modulus were measured. An assumption is made that hydrogen bonds involved in crimping are weakened in water.

B. Technology--Process and Product Development

1. Improved Mechanical Knitting Technology. We are studying methods for spinning shrink-resist-treated top and for weaving or knitting the yarn into washable apparel. Studies of dimensional properties have shown that all knitted constructions can be dimensionally specified by parameters similar to those developed for the plain knitted structure, if the "structural knit-cell" is defined. This suggests that the configuration in space of the knit-cell is a geometrically determinate form which is independent of fabric construction. For the parameters to apply, the fabric must be in a state of minimum internal energy, which is achieved only after wet mechanical agitation. Even then, the dimensional

parameters are not strictly constant but depend on the ratio of loop length to yarn diameter. For plain knitted structures in a fully relaxed state, a fabric thickness has been defined by a dimensional parameter which is independent of loop length and proportional to yarn diameter. The degree of fabric compactness is highly dependent on loop length, and less dependent on the state of relaxation.

2. New Yarns and Fabrics of Wool and Mohair Combined with Other Fibers.

We are conducting research to develop blends with optimum functional properties, and processing and finishing procedures for them. Worsted fabrics of blended wool and cotton (50/50, 60/40, 70/30, 80/20) were produced, WURLAN shrink-resist treated, processed by delayed-cure cellulosic crosslinking and evaluated for durable press performance. WURLAN treatment of top before blending produced a more acceptable handle than treatment of the blend fabric. For satisfactory durable press, at least 40% cotton is required. Strength and abrasion resistance of resultant durable press-treated fabric are marginal, particularly in a light-weight fabric. Woolen system tri-blend fabrics of wool/cotton/nylon and wool/high wet modulus rayon/nylon (50/40/10 and 65/25/10) were manufactured, and durable press performance was evaluated. Both blend levels containing rayon produced satisfactory durable press garments, whereas with the blends containing cotton at least 40% cellulosic was required. A minor amount of nylon raised the strength and abrasion resistance to acceptable levels. These results define the maximum wool content consistent with adequate durable press performance. Durable press garments containing wool will be marketed in the near future.

We have completed a project to find new approaches for the chemical and physical modification of coarser wools as a basis for development of improved yarns and fabrics that would increase markets. Significant accomplishments include an improved procedure for shrink-proofing wool fabric with ozone, a novel electrical discharge method for continuous treatment of wool in webbing form, and a new method for making high stretch yarn.

The reaction of wool with ozone has been extensively investigated in terms of antifelting and bleaching effects. The reaction rate of ozone with wool can be increased by mixing steam with the ozone and passing the mixture through, rather than over, the wool. Although this method shortened the required reaction time, ozone consumption proved excessive, and the wool was seriously degraded.

High reaction rate with minimum wool damage and lower ozone consumption can be achieved by passing the dry ozone gas over fabric with a controlled moisture regain of 30 - 40%. This moist wool-ozone reaction can be further improved by increasing the surface velocity of the gas stream over the fabric with simultaneous contact heating of the underside of the fabric.

All wool stretch yarn has been produced by a twist, set, untwist procedure. Setting of the coiled configuration has been achieved by various resin treatments. The most promising resin setting procedures involve application by interfacial polymerization or phase boundary crosslinking techniques and solvent application of a reactive polyolefin. These methods impart a helical form to yarns producing an elastic property which is permanent to repeated load cycling and to repeated wetting and drying. However, the permanence of the stretch is lost by exposure to prolonged boiling. Recent investigations of combined heat setting (with water at 240° F.) and resin setting has produced yarns which retain stretch properties after prolonged boiling in water.

Further developmental studies of these promising new techniques for imparting desired improved functional effects on wool yarn and fabrics are under way. These investigations include design of experimental processing equipment for continuous treatment of carded webbing, top, yarn and fabric.

PUBLICATIONS -- USDA AND COOPERATIVE PROGRAMS

Chemical and Physical Investigations to Improve Products

- Araki, K., Kiho, H., and Stannett, V. 1966. The kinetics of heterogeneous mutual radiation grafting. *Die Makromolekulare Chemie* 95:106-16. (Contract)
- Corfield, M. C., Fletcher, J. C., and Robson, A. 1967. Amino acid sequences of peptides from a tryptic digest of a urea-soluble protein fraction (U.S.3) from oxidized wool. *Biochem. J.* 102:801-14. 1/
- Darbari, G. S., Singh, R. P., and Verma, G. S. 1965. Anomalous acoustic absorption in mixtures of glycerol and water at 0.8 MC/S. *Physics Letters* 18(2):119-20. 1/
- Darbari, G. S., Singh, R. P., and Verma, G. S. 1966. Temperature dependence of ultrasonic absorption in mixtures of glycerol and water. *Il Nuovo Cimento, Serie X* 41:15-24. 1/
- Fong, W., Miller, L. A., Ash, J. F., Ingenthron, W. W. Jr., and Lundgren, H. P. 1965. Development of a continuous WURLAN treatment for wool top. *Proc. Third Internatl. Wool Textile Res. Cong. Paris, Sec. 3*, pp. 417-31.
- Forslind, B. and Swanbeck, G. 1966. Keratin formation in the hair follicle. I. An ultrastructural investigation. *Expt. Cell Res.* 43(1):191-209. 1/
- Fourt, Lyman. 1966. Improvement of luster of wool fabrics. *Textile Res. J.* 36(10):915-24. (Contract)
- Fourt, Lyman. 1966. Scale angles for wool and mohair. *Textile Res. J.* 36(10):899-902. (Contract)
- Gervasi, J. A. and Stannett, V. 1966. Studies of the chemical modifications of wool and their effects on the wool-water relationship. Part I. Chemical modification of wool. *J. Appl. Polymer Sci.* 10:1217-28. (Contract)
- Heidemann, G. and Halboth, H. 1967. X-ray evidence of regularly distributed lysine in alpha-keratin. *Nature* 213:71-72. 1/
- Jones, Francis T. 1967. Refractive index determination for liquids by crystal rotation. *The Microscope & Crystal Front* 15(8):309-13.
- Koenig, N. H. and Crass, R. A. 1966. Isocyanate and beta-propiolactone treatment of wool. U.S. Patent No. 3,282,640.
- Koenig, N. H. 1966. Epichlorohydrin and acid anhydride treatment of wool. U.S. Patent No. 3,285,691.

1/ Research supported by P.L. 480 funds.

- Launer, Herbert F. 1966. Effect of light upon wool. Part VI: Spectral conformity in photobleaching of wool. Textile Res. J. 36(7):606-11.
- Lundgren, Harold P. 1966. Some new developments in wool modification. Proc. 10th Canadian Textile Seminar (International), Kingston, Ontario, pp. 104-110.
- Lundgren, H. P. and Pardo, C. E., Jr. 1966. Process for preventing yellowing of moist raw wool through treatment with formaldehyde. U.S. Patent No. 3,282,639.
- Lundgren, Harold P. 1965. Role of alkali salts in the heat stability of wool. Institut Textile de France, Paris.
- Medley, J. A. 1966. Structure of water-swollen keratin in relation to the diffusion of various types of molecule. Proc. Wool Textile Research Congress (International), Institut Textile de France, Paris. 1/
- Needles, H. L. 1967. Crosslinking of gelatin by aqueous peroxydisulfate. J. Polymer Sci. Part A-1, 5:1-13.
- Needles, H. L. 1967. Crosslinking of silk fibroin by aqueous peroxydisulfate. J. Appl. Polymer Sci. 11:719-26.
- Needles, H. L. 1967. Riboflavin-sensitized photopolymerizations of acrylic monomers in the presence of proteins or amino acids. J. Polymer Sci. B, 5(7):595-600.
- Needles, H. L. and Ivanetich, K. 1967. Decarboxylation of N-acetylamino-acids with lead tetra-acetate in N,N-dimethylformamide. Chem. and Industry 4:581.
- Pittman, A. G., Wasley, W. L., Whitfield, R. E., and Remy, D. E. 1965. Reactive polymer finishes for wool. II. Polysiloxanes, fluoroalkyl acrylates and polyethylene imine. Institut Textile de France, Paris, Sec. 3, pp. 407-16.
- Pittman, A. G., Sharp, D. L., and Lundin, R. E. 1966. Polymers derived from fluoroketones. I. Preparation of fluoroalkyl acrylates and methacrylates. J. Polymer Sci. A-1, 4:2637-47.
- Pittman, A. G. and Sharp, D. L. 1966. Fluoro ketone-metal fluoride adducts as fluorinating agents in the preparation of fluorosilanes and fluorinated acyl fluorides. J. Org. Chem. 31:2316-8.
- Pittman, A. G. and Wasley, W. L. 1967. Process of treating textiles with perfluoroacyl bis-aziridine compounds. U.S. Patent No. 3,300,274.

1/ Research supported by P.L. 480 funds.

- Scherer, J. R. 1967. A transferable force-field for out-of-plane vibrations of chlorinated benzenes. *Spectrochimica Acta* 23A(5):1489-97.
- Stigter, D. 1967. On density, hydration, shape, and charge of micelles of sodium dodecyl sulfate and dodecyl ammonium chloride. *J. Colloid and Interface Sci.* 23(3)379-88.
- Tomimatsu, Y., Vitello, L., and Gaffield, W. 1966. Effect of aggregation on the optical rotatory dispersion of poly(α ,L-glutamic acid). *Biopolymers* 4(6):653-62.
- Wasley, William L., Pittman, Allen G., Whitfield, Robert E., and Remy, David E. 1965. Reactive polymer finishes for wool. I. Polyamides, polyurethanes and polyethylene derivatives. *Institut Textile de France, Paris, Sec 3*, pp. 397-406.
- Whitfield, R. E. and Needles, H. L. 1967. Crosslinking copolymers containing N-methylcarbanyl radicals. U.S. Patent No. 3,314,909.
- Williams, J. L., Stannett, V., and Armstrong, A. A., Jr. 1966. Studies of the chemical modifications of wool and their effects on the wool-water relationships of modified and unmodified wool. *J. Appl. Polymer Sci.* 10:1229-45. (Contract)

Technology--Process and Product Development

- Knapton, James J. F. 1966. The dynamics of weft-knitting: a mathematical analysis. *Textile Res. J.* 36(8):706-14.
- Knapton, James J. F. 1966. The dynamics of weft knitting and the measurement of wool yarn knitting performance. *Knitted Outerwear Times* 35(42): 17-19, 101, 103.
- Knapton, James J. F. and Munden, Dennis L. 1966. A study of the mechanism of loop formation on weft-knitting machinery. Part II. The effect of yarn friction on yarn tensions in knitting and loop formation. *Textile Res. J.* 36(12):1081-91.
- Knapton, James J. F. 1967. Characteristics of fibre friction. *Nature* 213(5079):898-99.
- Knapton, James J. F. 1967. New design aspects of weft knitting machinery. *Knitted Outerwear Times* 36(8):21-23.
- Lundgren, Harold P. 1966. Modernizing wool - A realizable mission. In "Synthetics and substitutes for agricultural commodities," proceedings of a symposium, pp. 20-31.

O'Connell, R. A., Krasny, J. F., and Russell, H. W. 1967. Distortion angle and constructional factors of woolen and worsted fabrics. Textile Res. J. 37(1):58-59.

Russell, Harold W. 1966. Simplified fabric analysis. Textile Indus. 130(9):183-5.

AREA NO. 6. CITRUS AND SUBTROPICAL FRUIT UTILIZATION - FOOD

Problem. The economic stability of the citrus and subtropical fruit industries in the Western Region is dependent upon effective utilization of fruit that cannot be accommodated on the fresh fruit market. The utilization of surplus or wholesome but blemished fruit provides the margin necessary to assure adequate returns to the farmer and continued development of stable markets. Ineffective utilization of products and continuously increasing processing costs are resulting in decreased returns to the growers. The California-Arizona grapefruit industry is encountering difficulty in disposing of both fresh fruit and processed grapefruit products. The pineapple and subtropical fruit industry in Hawaii must find practical methods for processing its products for export in order to prevent the accumulation of burdensome surpluses. The navel orange industry in California is hampered by the unavailability of satisfactory processes for the utilization of navel oranges. Juice extracted from early fruit, and during some seasons from almost all of the navel oranges, contains substances that impart an intolerable bitter flavor to juice products after mild heat-processing or after standing at ambient temperature for a short time. Large new plantings of navel oranges may be expected to aggravate the utilization problem. Deterioration of the flavor and color of these and other processed citrus and subtropical fruit products imposes severe limitations upon the economic stability of the industry.

Information is needed on the chemical composition of citrus and subtropical fruits and their products and byproducts as a basis for the development or application of new and improved methods of processing and for the production of new and improved food and industrial products and pharmaceuticals. Special attention needs to be given to the nature of the chemical changes involved during pre-treatment, processing and handling which lead to the formation of off-flavors, -colors, and -odors in processed products.

USDA AND COOPERATIVE PROGRAMS

In the Western Utilization Research and Development Division, a concentrated program of fundamental research on citrus and subtropical fruit and its application to industry problems is conducted at the Division headquarters at Albany, California; at the Fruit and Vegetable Chemistry Laboratory in Pasadena, California; at the University of Hawaii, Honolulu; by contracts at Riverside, California, and Tucson, Arizona and under P.L. 480 in India. Investigations are conducted on the composition of citrus essential oils, the flavonoid compounds and other citrus constituents that are related to off-flavors and darkening of citrus products, the natural flavor components of oranges, the enzyme systems that are involved in the appearance or disappearance of constituents and structures of plant tissues, and the constituents of dates that affect the quality and stability of products. The findings of such research are applied in the development of new and improved citrus, tropical, and subtropical fruit products.

The Federal program of research in this area totals 10.6 scientist man-years, including contract research. Of the total, 1.7 are assigned to investigations on chemical composition and physical properties; 3.3 on flavor; and 5.6 on technology--process and product development. The Division supervises one research project supported by a P.L. 480 grant.

PROGRAM OF STATE EXPERIMENT STATIONS

A total of 23.4 scientist man-years is devoted to this area of research.

PROGRESS -- USDA AND COOPERATIVE PROGRAMS

A. Chemical Composition and Physical Properties

1. Lemon Oil and Juice Products of Improved Stability. We are conducting research to determine the relationship of the constituents of lemon to the flavor, color, and stability of products.

Ultraviolet-fluorescing compounds in cold-pressed lemon and lime peel oils were separated by thin-layer chromatography (TLC) into patterns distinctly different from those of cold-pressed bergamot, orange, grapefruit and tangerine peel oils. To differentiate between lemon and lime oils, two-dimensional TLC was employed. Also, we tested several methods of isolation and analysis of nucleic acids and nucleotides of lemon juice. A study of the effects of the preservatives, sulfur dioxide, benzoate and sorbate, and storage conditions on the analytical procedures developed to characterize lemon juice indicates that published methods may be used except for formol titration where the aliquot must be boiled 1 min. to expel sulfur dioxide. The B peak used to determine the phenolic content of the juice is not affected by addition of sorbate. Amounts of citric acid, amino acids, malic acid, and total phenolics remain constant up to 118 days' storage at 20° C.

At the University of Baroda in India, a study of carbohydrate metabolism and formation, and the accumulation and breakdown of organic acids in citrus is supported by P.L. 480 funds. To test the hypothesis that organic acids in citrus fruits originate by enzymic conversion from carbohydrate in fruit vesicles, lemons (Citrus acida) were studied to determine the sites of enzymes and intermediates concerned with glycolysis and ascorbic acid synthesis. Outer skin, inner skin, vesicles and fruit juice were analyzed. All areas of the lemon appear to possess metabolic systems to synthesize ascorbic and citric acid.

2. Date Composition and Products. Three systems are involved in the darkening of dates: sugar browning, enzymic oxidative browning of phenolic constituents, and nonenzymic oxidative browning of tannins. Under a recently completed project, we have determined that the main enzymic browning substrates in dates are three isomeric monocaffeoylshikimic acids. All are newly discovered compounds not found in other common fruits. Numerous flavans also occur in

small amounts in immature dates (but not in mature dates) and all are enzymic browning substrates. One of these, shown to be epicatechin, disappears during fruit maturation, suggesting that it may be partly responsible for the characteristic golden-brown color of ripe dates.

Our research on the three main browning systems of dates indicates the role played by each during ripening, processing and storage. As the green date softens during ripening, the concentration of phenols decreases as a result of enzymic browning, and the fruit becomes light-brown. Later in the season when the fruit dries on the palm, the browning enzymes are probably inhibited by the low moisture content so that enzymic browning is slowed. Thus, dry fruit having a very light or slightly greenish color has probably dried to a low moisture content before sufficient enzymic browning could take place. After hydration and an intermediate storage period, the fruit is medium brown, and the phenolic-enzymic-browning substrates are no longer detectable. Thus, it appears that enzymic browning of naturally occurring phenols is mainly responsible for the brown color of ripe dates and also contributes somewhat to browning during processing and early storage. It does not appear to be responsible for the very dark color of dates stored a long time.

Because their reaction rates are slow at normal temperatures, tannin browning and sugar browning appear to be most important during heat processing and during storage after processing. Brown-pigment precursors probably form during heating and lead to brown pigments during subsequent storage.

Since color is most easily developed during heat processing, this step affords the best opportunity to achieve color uniformity, but improper heat processing, particularly the use of high temperatures, can be detrimental. Because color is most stable in dry dates, field-dry fruit is best for storage. Once the fruit is hydrated, color begins to darken, and fruit stored for different periods differ in color. The small color variations of fruit stored dry can be largely equalized by controlled heat processing. High quality dates, which usually require little or no hydration, frequently have a greenish cast and color variability that can be improved by a short heat treatment at about 120° F. Reddish off-colors sometimes occur in dry dates that required long hydration and processing periods. These off-colors can be prevented by avoiding temperatures above 140° F.

The date industry has repeatedly observed that some processed dates attain a better flavor than others, but the reasons were not known. We found that dates increase in acidity during processing, and since flavor may be related to acidity, we investigated treatments, such as heat, that increase the acidity. By carefully controlling time, temperature, and moisture content, we achieved appreciable flavor enhancement. In dates at 22-28% moisture, flavor was easily enhanced, but it was difficult in dates at low moistures (14%). Temperatures above 140° F. were detrimental to flavor, but 120° F.

was beneficial. Dates with 22% moisture reached optimum flavor in 3 days at 120° F.; longer treatment produced off-flavor. The flavor of diced dates, generally quite weak, can be greatly improved by holding the product 3 to 5 days at 100° F. The industry now uses this process. All of these treatments increased the acidity of date tissue,

To determine why the acidity of dates increases during processing, we studied the organic acids of dates. In immature fruit, malic acid represented about 75% of the ether-soluble acids. Other free acids included phosphoric, citric, and galacturonic. Bound acids included shikimic, glycolic, and galacturonic, together representing about 4% of the total ether-soluble acid fraction. Quinic acid was not detected. The unique presence of caffeoyl-shikimic acids in dates appears to be related to the presence of shikimic acid and absence of quinic acid, an unusual circumstance since most common fruits contain significant amounts of quinic acid. Although the acids of processed dates remain to be determined, it appears that enzyme hydrolysis of bound acids (including those not soluble in ether) may be responsible for the increasing acidity during processing and storage.

B. Flavor

1. Control of Bitterness in Navel Orange Juice and Concentrates. The Stanford Research Institute at South Pasadena, California is conducting contract research to develop a practical rapid assay method to measure individual limonoid constituents. Industry needs such a method to help control the bitterness of navel orange products,

An analytical procedure for determining limonin in citrus juice has been simplified to make it more suitable for routine use. The procedure has been used to measure the limonin content of freshly squeezed navel juice, aged juice, and commercial juice and concentrate. The juices were also evaluated by a taste panel to determine their degree of bitterness. Good correlation was obtained between bitterness and limonin content. The taste threshold for limonin was 4 to 5 ppm. Navel oranges on Trifoliate rootstock seem to develop less bitterness than those on Troyer or Cleo rootstocks. The limonin in navel oranges is concentrated (78-98%) in the peel, rag and seeds.

2. Sweeteners from Citrus Concentrates. We are investigating the flavonoids and bitter terpenoids of citrus fruits, particularly navel oranges. A new sweetener, hesperetin glucoside dihydrochalcone, has been prepared starting with the hesperidin flavonoid. It has about the same sweetness as naringin dihydrochalcone, but its sweetness is less clinging. Since hesperidin is the cheapest and most accessible citrus flavonoid, a sweetener prepared from it may be economically more attractive than the earlier dihydrochalcone sweeteners. The bitter flavonoid naringin can be converted directly to neohesperidin dihydrochalcone, the sweetest dihydrochalcone in this series. A new flavanone, eriodictyol neohesperidoside, has been isolated from Seville oranges.

Studies on the photochemistry of limonin have shown that it can be converted to two photoproducts, photolimonin I and II, which have little or no bitterness. The structures of these compounds have been determined. The photochemical conversion of bitter limonin to tasteless (or nearly tasteless) photoproducts suggests a possible route for debittering navel orange juice. The structure of another naturally occurring limonoid, rutaevin, has been determined as 6-keto-epilimonol.

C. Technology--Process and Product Development

1. Concentrates and Powders from Hawaiian Fruit. The development of concentrated Hawaiian fruit products would reduce packaging and transportation costs, build mainland markets, and help diversify Hawaiian agriculture. At our Hawaii field station, we are studying methods to reduce the bulk and weight of tropical and subtropical fruits while retaining high quality. Banana puree stabilized by addition of 200 ppm. sulfur dioxide, heat inactivation of enzymes, and addition of citric acid and 100-200 ppm. potassium sorbate has retained its original high quality for at least 3 months at 35-40° F. Taste panel tests showed that 250 ppm. sorbate may affect the flavor adversely but 100 ppm. was not detected. The puree made from Hawaii-grown bananas would be suitable for use in bakery and dairy products. Five hybrids each of guavas and passion fruit were processed into beverage products for quality evaluation to assist in selection of varieties for expansion of commercial acreage. Inactivation of enzymes in passion fruit juice by rapid heat exchange enhanced the quality of the juice. Stability of papaya nectar, passion fruit nectar and guava jelly held at 35° to 100° F. is being evaluated by taste panels. Guava jelly at 100° F. deteriorates rapidly, about 11 times faster than jelly at 55° F.

Research at the Instituto de Investigaciones Technologicas, Bogota, Colombia, supported by P.L. 480 funds has been concluded. Thirty-seven compounds were identified in guava essence and 18 in that of curuba. However, none of these compounds possessed the characteristic aroma of the fruits. Several attempts were made to "lock-in" the essences into natural inert carriers. To "lock-in" the essences, the processes which required low temperatures or very short times of operation gave better results. The stability during storage and ability to subsequently restore the aroma was dependent upon the kind of carrier and type of process followed to enclose the essence.

2. Use of California-Arizona Desert Grapefruit in Juice Blends and as an Acidulant in Food Manufacture. We are conducting research to isolate, identify and characterize nitrogenous compounds, carbohydrates and flavonoids that affect the color or flavor of desert grapefruit grown under known conditions. Also we are investigating the metabolism of these compounds, changes in them during processing, and the physiological activity of selected compounds. The data obtained will be a guide for processors in improving grapefruit products, pharmacologists in evaluating reputed physiological

activity, and plant breeders in developing varieties suited to processing. A previously unrecognized compound in grapefruit was isolated and identified as dihydrokaempferol. It co-occurs with naringenin and kaempferol (following hydrolysis) in all actively metabolizing grapefruit tissues studied, including very young fruit, young growing leaves, and young twigs. This finding supports the postulated biosynthetic pathway: flavone $\rightarrow$ dihydroflavonol $\rightarrow$ flavonol. In our investigation of grapefruit color changes, we found that the green peel of Marsh grapefruit and green plants contain the same major carotenoids. However, as the fruit ripens, its chlorophyll disappears and carotenoids accumulate. Comparison of mature early and mature mid-season fruit showed that inhibition or blockage between phytoene and phytofluene prevents the formation of colored carotenoid pigments. The nature of this inhibition is not yet known but it is, apparently, the reason for the light color of ripe desert grapefruit.

In contract research at the University of Arizona in Tucson, new food products using desert grapefruit and blends of grapefruit with other foods are being developed. Grapefruit plus juice packaged in glass containers, heated to 185° F., cooled rapidly, and stored at 40° F. or below had a shelf-life of well over 6 months with little or no off-flavor from heating. Grapefruit juice blended with peach and apricot juices and vacuum packed in enamel-lined cans retained color and flavor for long periods at 40° and 80° F. Blends of grapefruit juice with juices from frozen strawberries, raspberries, boysenberries, and olallieberries continue to enjoy high acceptance. These blends are most stable in glass containers, but they do not have long shelf-lives at high temperature. Blends of guava puree and grapefruit juice appear promising. Apricots canned with 10-20% of grapefruit juice in the sirup retained their color and flavor for over a year. Addition of grapefruit juice to apricots and peaches appears to enhance the flavor of both canned fruits and nectars. Grapefruit juice as normally prepared has a bitter flavor at limonin levels from 8-12 ppm. Juice prepared to avoid incorporation of juice sacs, membranes, and peel juice appears to have considerably lower limonin levels.

A second contract research program at the University of Arizona, Tucson will seek to improve the quality, convenience and stability of Arizona-California desert grapefruit products.

3. Processing Mechanically Harvested Dates. The University of California at Riverside is conducting contract research to improve the quality of mechanically harvested dates. In comparing tender and tough dates they found that tough dates have a lower moisture content and lower glucose and fructose levels, but a higher sucrose level. Total sugar contents of tough and tender dates are similar, as are pectin fractions, lignin content, hemicelluloses, cellulose, and nitrogen assays of 80% ethanol extracts and residues. Mesocarp parenchyma cell walls become highly disorganized as the fruit ripens. The degree of disorganization is not as pronounced in tough dates as in tender dates, which may account for the toughness of the drier dates.

We are conducting research to develop economically feasible methods for processing mechanically harvested dates, which vary widely in degree of maturity. Dates harvested in 1966 at three stages of maturity were separated by differential flotation in sucrose solutions of various concentration. Then they were frozen at 0° F. and held 1 to 3 days. This temperature was used because at 15° F. freezing was incomplete and at -20° F. ripening was not induced. After freezing, the dates were tempered 2 to 3 days at 34° F. During tempering, they began to take on a translucent appearance indicative of ripening. After tempering they were exposed to air ranging from ambient temperature to 120° F. Ripening was less satisfactory (except in some more mature grades) at higher temperatures, perhaps because of dehydration. Separations have also been made of dates fully ripened on the palm (corresponding to those now received at processing plants). A diverging roller separator was developed that eliminates unpollinated and cull dates and separates the remainder into three size grades, which are then separated by differential flotation in water to give six grades.

PUBLICATIONS -- USDA AND COOPERATIVE PROGRAMS

Chemical Composition and Physical Properties

- Donohue, H. V., Lowry, Larry K., Chichester, C. O., and Yokoyama, Henry. 1966. The structure of neoxanthin. Chemical Communications (London) No. 21:807-8.
- Fisher, J. F., Norby, H. E., Waiss, A. C., Jr., and Stanley, W. L. 1967. A new coumarin from grapefruit peel oil. Tetrahedron 23(6):2523-28.
- MacLeod, Wm. D., Jr. and Buigues, Nelida M. 1966. Lemon oil analysis. I. Two-dimensional thin-layer chromatography. J. Food Sci. 31(4): 588-90.
- MacLeod, Wm. D., Jr., McFadden, W. H., and Buigues, Nelida M. 1966. Lemon oil analysis. II. Gas-liquid chromatography on a temperature-programmed, long, open tubular column. J. Food Sci. 31(4):591-4.
- Stanley, W. L. and Vannier, S. H. 1967. Psoralens and substituted coumarins from expressed oil of lime. Phytochem. 6(4):585-96.
- Vandercook, Carl E. and Stephenson, Rebecca Garner. 1966. Lemon compounds. Lemon juice composition. Identification of the major phenolic compounds and estimation by paper chromatography. J. Agr. Food Chem. 14(5):450-4.
- Yokoyama, Henry and Vandercook, Carl E. 1967. Citrus carotenoids. I. Comparison of carotenoids of mature-green and yellow lemons. J. Food Sci. 32(1):42-8.
- Yokoyama, Henry and White, Michael J. 1966. Some aspects of carotenoid pigment formation in the desert grapefruit. The Citrus Industry 47(12): 28,30.
- Yokoyama, Henry and White, Michael J. 1966. Citrus carotenoids V. The isolation of 8'-hydroxycitranaxanthin. J. Org. Chem. 31(10):3452-4.
- Yokoyama, H. and White, M. J. 1966. Citrus carotenoids. VI. Carotenoid pigments in the flavedo of sinton citrangequat. Phytochem. 5(6):1159-73.

Flavor

- Dryer, David L. 1966. Citrus bitter principles. VI. Ichangin. J. Org. Chem. 31:2279-81.
- Dryer, D. L. 1966. Constituents of *Thamnosma Montana* Torr and Frem. Tetrahedron 22:2923-7.

Gentili, Bruno and Horowitz, Robert M. 1965. Isolation and characterization of some new flavonone rutinosides. Bul. Natl. Inst. Sci. India No. 31: 78-82.

Hornstein, Irwin and Teranishi, Roy. 1967. The Chemistry of Flavor. Chem. & Eng. News 45(15):92-108.

Ikedo, R. M., Stanley, W. L., Vannier, S. H., and Rolle, L. A. 1966. Production of full-flavored stable essential oils. U.S. Patent No. 3,294,550.

Maier, V. P. and Metzler, D. M. 1967. Grapefruit phenolics I. Identification of dihydrokaempferol and its co-occurrence with naringenin and kaempferol. Phytochem. 6(5):763-65.

Technology -- Process and Product Development

Bomben, John L., Mannheim, H. Chaim, and Morgan, A. I., Jr. 1967. Operating conditions for aroma recovery by new vacuum stripping method and evaluation of aroma solutions. Fruchstift-Industrie 12(2): 44-53.

Brekke, John E. and Allen, Lyle. 1966. Banana dehydration. Hawaii Agricultural Experiment Station Technical Progress Report No. 153.

Cavaletto, C., Dela Cruz, A., Ross, E., and Yamamoto, H. Y. 1966. Factors affecting macadamia nut stability. I. Raw kernels. Food Technol. 20(8):108-11. (Contract)

Curl, A. Laurence. 1967. Apo-10'-violaxanthal, a new carotenoid from Valencia orange peels. J. Food Sci. 32(2):141-43.

Dela Cruz, A., Cavaletto, C., Yamamoto, H. Y., and Ross, E. 1966. Factors affecting macadamia nut stability. II. Roasted kernels. Food Technol. 20(9):123-4. (Contract)

Mannheim, H. C., Bomben, J. L., Guadagni, D. G. and Morgan, A. I., Jr. 1967. Evaluation of orange aroma solutions obtained by a new vacuum stripping method. Food Technol. 21(3A):51-55.

Popper, K., Notter, G. K., and Nury, F. S. 1966. New products from coconut - non-dairy chip dips and cream cheese. Food Processing/Marketing 27(12):9296-8.

Rockland, Louis B. 1966. Factors affecting the stability of raw and roasted macadamia nuts: A summary of USDA-supported research at the University of Hawaii. Calif. Macadamia Society Yearbook.

Stafford, Allan E., Cavaletto, Catherine G., and Brekke, John E. 1966.
Hawaii Experiment Station Technical Progress Report No. 157.

Tonaki, Keith, Brekke, John and Frank, Hilmer. 1967. Banana Puree.
Univ. of Hawaii Extension Service Circular 418.

Yokoyama, H. 1967. Carotene derivatives and use thereof. U.S. Patent
No. 3,321,315.

AREA NO. 7. DECIDUOUS FRUIT AND TREE NUT UTILIZATION - FOOD

Problem. Fruits and nuts are valued for their unique flavor, color, and mineral and vitamin content. In the period of abundance at harvest time, markets are glutted and growers often do not get an adequate return. Crops are perishable, and processing to preserve their unique qualities is difficult. No processed fruit retains completely the fresh values, although many highly acceptable products exist and about half of the fruits and nuts marketed in the United States are processed. Processing makes these commodities available to consumers the year around, and has opened new markets for producers. The proportion of processed commodities is steadily increasing but is dependent upon a continuing flow of new knowledge. Processing to preserve color, flavor, texture, and nutrients presents many problems, and each new product requires the application of much scientific and technological skill.

The continued supply of preserved fruits is largely dependent upon relatively inexpensive sources of raw material. Decreasing supply and increasing cost of harvest labor is leading rapidly to the development of mechanical harvesting methods. Mechanical harvesting does not allow the sorting and careful handling of traditional hand picking. The processor must deal with trash, and bruised, cracked, immature, and over-ripe fruit along with prime quality. Research is necessary to develop new processes and products to reduce costs and utilize such raw material in the processing plant.

The freezing process for preserving certain fruits keeps products at near fresh fruit condition, but many problems remain unsolved. The enzymatic browning of frozen peaches and the sloppy texture of frozen strawberries on thawing are two examples.

Frozen fruits require expensive low-temperature storage and transportation facilities. This expense can be greatly reduced by removing a portion of the water from the products. Orange and other fruit juice concentrates are well established in U.S. markets, and dehydrofrozen apple slices (rapid drying to 50% bulk weight and then freezing) are just becoming well established. Many other fruits and fruit juices should be amenable to concentration. Any frozen product, however, is not as well adapted for export as those which do not require refrigeration.

Maximum weight reduction, as well as less restrictive storage requirements, can be achieved through dehydration. The drying of fruit juices has been successfully accomplished by the vacuum puff drying and foam-mat drying processes. New methods are being developed to dehydrate pieces of fruit with excellent retention of color and flavor. Extension of laboratory procedures to pilot- and commercial-scale operations must still be done.

Flavor recovery and the incorporation of recovered flavor in solid carriers for addition to the dried products require technological and basic chemical

study. Aroma recovery techniques developed for fruit juice concentrates are being improved but require more work. Dried fruits are now widely used in the U.S. and abroad. Their popularity would grow if stable, higher moisture dried fruits were available and if lower levels of sulfur dioxide could be used without loss of quality.

Container costs for canned fruits limit the shipment of these products overseas. A solution of the container problem may be found in the use of lightweight fiber, foil, or plastic containers and aseptic filling procedures.

Fruit growers need new varieties of tree fruits and berries suited to processing and resistant to diseases endemic to each region of production. Utilization research is required in cooperation with farm research to assure growers of a market for fruit in the processing industry.

USDA AND COOPERATIVE PROGRAMS

In the Western Utilization Research and Development Division, a broad program of basic and applied research on deciduous fruits and tree nuts is conducted at the Division headquarters at Albany, California; in field stations at Pasadena, California, and Puyallup, Washington; by contracts in Berkeley, and Los Angeles, California, Fort Collins, Colorado, Geneva, New York, and Chicago, Illinois; and by grant funds under P.L. 480 in Israel, Taiwan, Austria, Switzerland, and India. Fundamental research is conducted on fruit constituents associated with flavor, color, and texture of fruit products. The work includes development of laboratory tools to isolate and characterize components, investigation of such components as they occur naturally and as they are altered by operations involved in preservation, and study of the relationships between the components and the product values being preserved. Applied research is conducted to develop new and improved processes and products that will increase utilization of fruits and tree nuts, including the development of high-quality concentrated and dehydrated products and more stable shelled tree nuts and the selection of improved processing varieties. Pioneering research on plant enzymes is also conducted.

The Federal program of research in this area totals 31.7 scientist man-years, including five contracts. Of the total number, 5.0 are assigned to investigations on chemical composition and physical properties; 7.5 on flavor; 2.0 on color, texture and other quality characteristics; 2.2 on microbiology and toxicology; and 15.0 on technology--process and product development. In addition, the Division sponsors research on fruit by means of six P.L. 480 grants.

PROGRAM OF STATE EXPERIMENT STATIONS

A total of 38.5 scientist man-years is devoted to this area of research.

PROGRESS -- USDA AND COOPERATIVE PROGRAMS

A. Chemical Composition and Physical Properties

1. Novel Uses for Plant Enzymes in Processing and Maturation of Fruit.

We are conducting research in plant enzyme chemistry to obtain basic knowledge upon which to build entirely new or more advantageous ways to utilize plants and plant products.

We have demonstrated that localization of enzymic activity within plant cells is greatly influenced by age of the cell, temperature under which it is grown, and what it is fed. This work, done with plant tissue cultures, appears applicable to whole plants, and it indicates that we may be able to optimize desirable components of plant cells by appropriate choice of environmental conditions.

We found that glutaraldehyde alters enzyme activity, both in cells and in vitro. In the case of an acid phosphatase present in the nuclei of plant cells, glutaraldehyde activates this enzyme, both in the intact cell and in its isolated nucleus.

Life processes in plants, such as germination, growth, maturation, sex expression, flowering, reproduction, and senescence, are regulated by hormones. Many of these hormones, e.g., abscisins, gibberellins, and steroids, are synthesized by plants from isoprene units. The metabolism of radioactive kaurene, a precursor of gibberellins, was found to be altered under flower-inducing conditions in Japanese Morning Glory. Conversion of kaurene to steviol, a substance closely related to the gibberellins, was demonstrated in a shrub. Inhibitors of the biosynthesis of gibberellins stunt the growth of conifers.

The female sex hormone, estrone, was discovered in the seeds of date palm and pomegranate trees. Cholesterol, the starting material from which all steroids are synthesized in animals, was shown to have a similar function in plants. By administering radioactive cholesterol to growing plants, its conversion to pregnenolone (a progesterone precursor in both plants and animals), sapogenins, and two types of steroidal alkaloids (with 21 and 27 carbons) was demonstrated. New chromatographic techniques for steroids have been developed.

2. Rancidity Control in Walnuts. We have studied the chemical basis for rancidity development in nut meats. Cold-pressed oils obtained from fresh and rancid walnut kernels were stripped in a molecular still. Three fractions were obtained: odorless stripped oil containing glycerides and other non-volatile constituents, molecular distillate, and volatile components trapped at -60° C. Yields of molecular distillates and the intensities of rancid odors in the volatile fractions increased with the moisture content of kernels and time and temperature of storage. Odor of the volatile fraction obtained from fresh kernels was similar to that

of rancid kernels but of lower intensity, suggesting quantitative but not necessarily qualitative differences. The molecular distillate contained three groups of compounds: uncharacterized, highly polar compounds; free fatty acids; and fatty acid methyl esters. The last group of compounds has been individually characterized in natural oils for the first time. Unequivocal proof of their identities was obtained. Systematic analyses of oils obtained from moisture-adjusted kernels, stored for one year at various temperatures, showed that major changes occurred in the proportions of the three groups of compounds during storage. Variations among individual compounds within each group are being investigated.

B. Flavor

1. Improved Flavor of Apple Juice and Concentrate. We are conducting research to improve the flavor and flavor stability of apple juice and concentrates. WURVAC is a new process we have devised for recovering volatile flavors. Aroma components and some water vapor are removed from juices by boiling at reduced pressure. The mixture is condensed at low pressure and the aromas are separated from the water by vacuum stripping with an inert gas. Then aromas are reabsorbed into a cold, highly dispersed solvent at atmospheric pressure. Orange concentrates made with WURVAC aroma and peel oil added are more like fresh orange juice than those made by the cutback method and they are as stable.

Some fruit aroma volatiles, notably esters, can be removed from juices or concentrates by extraction with liquid carbon dioxide at room temperature and elevated pressures. A laboratory-scale extraction apparatus has been built and tested. Effectiveness of extraction increases from alcohols to aldehydes to ketones to esters, suggesting that anhydrous, alcohol-free flavor concentrate might be recovered without otherwise harming the juice.

We have identified fifty-six compounds in extract of commercial Delicious apple essence and have found that n-hexanal, 2-hexanal, and ethyl 2-methylbutyrate contribute significantly to aroma. Concentrations in 150-fold essence extract were 66, 295, and 4 ppm, respectively, but the first two compounds are not present in high concentration in fresh Delicious apple volatiles. Extraction efficiency of ether is most efficient, liquid carbon dioxide and charcoal are nearly as good, and the latter is excellent for extraction of alcohols. Fluorocarbon 114 and isopentane reject organoleptically unimportant low-molecular weight alcohols.

Supported by P.L. 480 funds, the Federal Research Station for Arboriculture, Viticulture and Horticulture in Wädenswil, Switzerland is studying enzyme systems and substrates and their effects on flavor and aroma of apple juice concentrate. Preliminary experiments on the influence of pectolytic enzymes on apple juice volatiles are underway. Volatiles from stored apples have been absorbed on activated carbon to study composition of emanations during preclimacteric and postclimacteric stages of maturation.

2. Improved Flavor of Canned Ripe Olives. Research aimed at controlling the development of off-flavors in the processing and storing of ripe olives for canning is being conducted by contract with the National Cannery Association's Western Laboratory in Berkeley, California. An expert taste panel from the olive industry could not agree on terms to describe various off-flavors in canned ripe olives. They could distinguish off-flavored samples from controls, but agreed descriptively only on metallic or bitter off-flavors. Olives held in brine for 20 to 30 weeks were judged superior to those stored for 15 or 40 weeks. Gas chromatograms of vapor from Mission, Manzanillo and Sevillano varieties were distinctly different, but differences could not be correlated with flavor. The pattern of change with time in volatile carbonyl compounds was determined. The content of polyunsaturated free fatty acids in raw olives decreased, but triglyceride-bound fatty acids changed little with brine storage of olives up to 40 weeks prior to lye-curing and canning.

C. Color, Texture and Other Quality Factors

1. Improved Stability of Apple Juice and Concentrate. The Colorado State University in Fort Collins is conducting contract research to eliminate cloud and sediment from apple juice. Sediment from clarified apple juice is a heterogeneous mixture relatively high in sodium. Bulk of the sediment is a polymer (molecular weight over 50,000) of protein-oxidized leucoanthocyanidin. Oxidation of leucoanthocyanidin may be minimized by treatment with salt and ascorbic acid during milling. Oxidized leucoanthocyanidin may be removed by filtration with polyamides prior to bottling. Plant runs have verified laboratory findings.

2. Improved Color and Stability of Fruit Products. We have initiated a study of the oxidative and light-catalyzed changes occurring in carotenoid pigments, and the oxidative, condensation, and complexing reactions of anthocyanins of fruits, to develop means for improving and stabilizing the color of fruit products.

We have completed a study of changes these anthocyanins and carotenoid pigments undergo during processing. Many flavylum salts decolorize in aqueous solution at pH 3-4 by reversible hydrolytic opening of the pyrylium ring to form chalcones. In fact, at pH 4-7 these flavylum salts exist largely (80-90%) in the form of those hitherto unsuspected chalcones. From these studies, the mechanism of sulfite bleaching of anthocyanins (a process of commercial importance, e.g., in the preparation of maraschino cherries) has been unraveled. The anthocyanin carbonium ion and bisulfite ion react to form a colored chromen-2-sulfonic acid. It may be possible to use certain synthetic flavylum salts closely related structurally to natural fruit pigments as yellow and orange colored substitutes for potentially carcinogenic azo dyes formerly used in food products.

We have shown that oxidation of flavylum salts at pH 5-7 actually yields phenolic 2-phenylbenzofurans. This discovery also has important applications

in fields unrelated to anthocyanin chemistry. 2-Phenylbenzofurans are physiologically active compounds with potency as great as that of vitamin E in preventing hemolysis of red blood cells by dialuric acid. We have prepared these compounds by simple oxidation of flavylum salts.

Coumestrol, the complex coumarino-benzofuran from alfalfa, is a potent estrogen responsible for infertility problems in cattle and sheep. Coumestrol and related compounds have now been synthesized by oxidation of 7,2',4'-trihydroxy-3-methoxy-flavylum chloride. The oxidation of flavylum salts to coumestrol and other 2-phenylbenzofurans requires the presence of alcohol. In its absence a new type of oxidation product is formed; the structures of these new products have been determined.

Flavylum salts rapidly condensed with phloroglucinol, resorcinol, and catechin (the most widespread natural polyphenol) to form crystalline dimers, the structure of which has been elucidated. This reaction is of great importance in suggesting one possible mechanism whereby dimeric flavonoids and tannins may be formed in plants. The surprising observation was also made during these condensation reactions, that considerable reduction of flavylum salts to colorless flavones occurs. Similar reduction of anthocyanin pigments, by reaction with co-occurring phenols, may thus be an important factor in anthocyanin decolorization,

Flavylum salts form colorless condensation products with reactive methylene compounds. Surprisingly, we found that certain flavylum salts form different products depending on the pH of the reaction mixture.

The reduction of a number of model flavylum salts with sodium borohydride, and with zinc and acid, has now been studied. Crystalline monomeric flav-2-enes are formed, as well as crystalline dimers. The structures of these dimers are complex and have not yet been elucidated.

The University of California at Los Angeles is conducting contract research on leucoanthocyanins and related phenolic pigments in fruits and their fate during processing. The work under this contract has led to the proposal of the structure of a naturally occurring proanthocyanidin and to proposals for a structural model for the condensed flavonoid tannins. Synthetic models have been prepared, the nature of which reinforce the belief that the hypotheses are sound. It is still necessary, however, to refine the evidence and to continue to study natural and synthetic proanthocyanidins. The materials studied up to this time have seldom been crystalline or homogeneous, probably because of stereochemical differences. Therefore, efforts are being made to prepare homogeneous, preferably crystalline compounds of the dimeric proanthocyanidin class in order to obtain further physical evidence for their structures.

Supported by P.L. 480 funds, the National Taiwan University in China is conducting a study of hemicelluloses and associated nitrogenous compounds. Hemicellulose plays a dominant role in the texture of bamboo shoots. Two

polysaccharides, a glucoxytan and an arabogalactan, appear to occupy the position in the cell wall architecture usually held by pectin. Carbohydrate analysis indicates that polysaccharides are synthesized from glucose in two ways: an independent reaction whereby glucose transfer yields cellulose, and a xylose transfer-dependent glucose transfer that yields glucoxytan. Different precursors are involved. ^{14}C -labeled and non-labeled sugar nucleotides are being synthesized by enzymic and organic syntheses.

P.L. 480 funds are also supporting research at the University of Delhi in India where a study of the chemical behavior of leucoanthocyanins in fruits is underway. Condensed leucoanthocyanidins were isolated from white grape seeds. A proanthocyanidin was recovered from the white grape peels. Only condensed leucoanthocyanidins were found in ripe fruits. Leucoanthocyanidins were recovered from apple juice and (in small quantities) from pears. As pears ripen, polymeric leucoanthocyanidins increase. Unripe fruits have lower polymers; the astringency of these fruits may be due to greater solubility of these substances.

Tannins and related polyphenolic polymers are responsible for the astringent flavor and cloud formation in clear juices. Existing methods for degrading these substances are drastic chemical procedures with undesirable side reactions. The Central Leather Research Institute in Madras, India, supported by P.L. 480 funds, is studying microbial and enzymic methods of degradation which might replace existing methods. The banana and cashew apple are under investigation. During ripening the free tannin content of bananas decreases. A comprehensive screening program was initiated to investigate the ability of microorganisms and plant enzymes to degrade tannins and other natural and synthetic polyphenols.

Supported by P.L. 480 funds, the Hebrew University in Jerusalem, Israel, is studying the nature, activity, and distribution of phenolases in deciduous fruits in order to minimize enzymic browning of products. Content of o-diphenyls and catechol oxidase activity were studied during apple development from fruit set to harvest. Content of o-diphenyls peaked early in development and then declined. Catechol oxidase activity peaked after that of the o-diphenyls. As fruit ripened, activity dropped sharply in particulate fractions. Browning rate in apple slices decreases with lowered enzyme activity. Sodium chloride inhibited activity in enzyme apple mitochondria. Increasing the sodium chloride concentration increased the inhibition. When the sodium chloride was removed by dialysis, the activity increased.

D. Microbiology and Toxicology

1. Control of Microbial Contaminants in Dried Fruits and Tree Nuts. We are conducting research to determine the sources of microbial contamination of concentrated fruit juices and methods for control. Heat-resistant molds were isolated from grapes and adjacent produce in the San Joaquin

Valley. Byssochlamys fulva exhibited the greatest heat resistance. Addition of 100 ppm. of sulfur dioxide reduced the heat resistance by 50% and precoat filtration reduced the asci and ascospore count by more than 99%.

Propyl p-hydroxybenzoate is an effective antimycotic agent for use on dates. Heat-treated raisin paste stored 6 months developed no objectionable off-flavor. A feasibility study indicates that some defective prunes can be sorted out electronically. Prune skins can be tenderized by combined heat and chemical treatments. Light colored, sulfur-free raisins have been produced by blanching Thompson seedless grapes before drying. Good flavored almond-fruit pastes with excellent texture have been prepared. If figs are refrigerated before grinding, a lighter colored fig paste results.

With P.L. 480 funds, the Institute of Biology and Agriculture in Vienna, Austria, is conducting research to discover physical or chemical methods of increasing irradiation sensitivity of yeasts and molds to reduce heat requirement for fruit juice pasteurization. They have found that conidiospores from different strains of Byssochlamys fulva differ markedly in resistance to irradiation. Ultrasonic treatment was better than other chemical and physical treatments to initiate spore germination in B. fulva. They have also found indications that magnesium ion is involved in spore germination.

E. Technology--Process and Product Development

1. Improved Wine and Juice Concentrates from Viniferous Grapes. Thompson seedless grapes, used for raisins, fresh fruit, and as a blending juice for wines, have been a surplus crop for a number of years. Methods for extracting a sediment-free juice would be useful for a number of new products, such as foam-mat dried powder and bland syrups. Improved extraction of flavor and color from red varieties of grapes would complement the work on white varieties in order to enhance the usefulness of possible blends. Thompson juice concentrates which have received insufficient heating in processing have been reported to contain the highly thermal stable mold organism, Byssochlamys fulva. Cooperative studies with the National Canners Laboratories have been conducted to determine optimum heating conditions and combined heating and chemical treatments for control.

We are conducting research to develop products from Thompson seedless and other viniferous grape varieties to increase markets. Verjuice, a potential blending acidulant, was prepared from unripe Thompson seedless grapes and preserved with diethylpyrocarbonate (DEPC). Harvesting of immature clusters will have the cultural effect of pruning. Peeled grapes can be dried osmotically against sugar or a hypertonic solution when an edible membrane is cast on the fruit. They rehydrate easily. Compounds isolated from Grenache grapes and identified included 1-hexanol, 3-methyl-1-butanol, trans-2-hexenal, hexenal and 1-heptanol. Mold infestation of cold storage rooms can be eliminated by spraying with DEPC. Waste processing waters

can be purified by passage over activated carbon and the chemical values returned to stream, thus effecting monetary savings and avoiding pollution.

Research aimed at improving the color and flavor of beverage juices from surplus viniferous grapes is underway. A rotating-drum countercurrent liquid-liquid extractor for emulsion-free extraction of wine components has been constructed. Wines directly fermented to high alcohol content were aged, after addition of fungal extracts, in straight and charred wood. With the latter, bourbon-type flavor developed in the wine. Growth of Aspergillus niger increases acidity of musts without a "musty" flavor if conidia growth is repressed. Electrolytic regeneration of ion exchangers for winery use shows substantial production savings and reduction of pollution. The method has been demonstrated to the industry. Biochemistry of Botrytis cinerea and its extracted enzyme systems was studied and new cultural methods investigated.

The mechanism of air oxidation of catechols and resorcinols to yield benzofurans appears similar to polymerization of polyphenols and tannins in grapes and wines. Two new bioflavones (hinokiflavone methyl ethers) have been isolated and identified from the leaves of Cryptomeria japonica.

Investigations are conducted under contract at the New York Agricultural Experiment Station in Geneva to develop better methods and materials for eliminating haze and precipitates in domestic wines so that they can compete in world markets. Protein-tannin complexes are held together by hydrogen bonding. The formation of the insoluble complexes is reversible and dependent on the ratio of tannin to protein in the mixture. The process can be reversed by adding a competing but non-precipitating simple phenolic compound and by heat. The size of insoluble particles can be kept small by adding tannin to gelatin solutions. More dilute solutions produce less precipitate. Water takes part in the reaction, as indicated by the effect of alcohol on tannin content of the precipitate. Loss of anthocyanin in tannin-protein systems is reduced by high tannin levels, indicating that competition for available sites on the protein exists between tannins and anthocyanins.

Contract research on the processing of viniferous grapes at the University of California in Davis has been concluded. A pilot scale "serpentine" press was developed for the continuous separation of juice from crushed white grapes. From tests with the prototype press, a commercial model has been built which should yield 150 gallons of juice per ton of Thompson seedless grapes.

A 3-stage countercurrent sugar extraction system was constructed and tested on a laboratory and commercial scale. The commercial unit, operated at 30 to 50 tons per hour on fermented and unfermented pomace, gave yields of 70 to 80% of theoretical equilibrium. Highest performance was achieved when the pomace was disintegrated.

Experiments on extraction of color of red grapes resulted in the development of a system for heating the grapes for short periods of time under 25 and 40 psig steam pressure. Various parameters, such as time, temperature, extent of fermentation, and aging were studied and optimum conditions were ascertained for different types of wine from numerous grape varieties. The extraction and identification of aroma materials from viniferous grapes were studied. Methods for flash steam heating gave results comparable to control samples. Eight Muscat-flavored grapes were analyzed by gas chromatography and the differences in types and quantities of volatile compounds were compared with the subjective evaluations of aroma.

2. Osmotic Concentration of Fruit Juices. Research is conducted to develop a method to dehydrate piece-form fruit having good flavor, color, stability, and other quality factors to increase markets. Excellent dehydrofrozen fruits were produced by osmotic dehydration in syrup to 50% weight reduction followed by freezing. Rehydration of these products was slow, but was much improved by cycling the fruit between boiling and cold water baths two or three times. Osmotically dehydrofrozen fruits can be further dehydrated at any time with no loss in quality.

Fourteen batches of Bartlett pears were osmotically dehydrated in succession in one lot of syrup. The syrup darkened slightly, but the pear color remained light. Syrup could be used indefinitely in this system since about 1/7 of the syrup was lost with each batch and made up with fresh syrup.

Sucrose and lactose inhibited polyphenol oxidase activity about 40% at 1 molar concentration. Other di- and tri-saccharides were ineffective, as were glycerol and ammonium sulfate. Monosaccharides were only half as effective as sucrose. Therefore, the inhibition is relatively specific and is not due to osmotic pressure alone.

In studies of moisture determination methods, raw fruit or powdered dried fruit was pressed into thin films, which greatly increased the rate of dehydration, but the last traces of moisture were difficult to remove. Addition of methyl alcohol as a water extractant showed promise, but the alcohol evidently replaced water in dried fruit since according to Karl Fischer titration, moisture content was reduced to zero but no equivalent weight loss occurred.

3. Evaluation of Processing Characteristics of Northwest Soft Fruit and Berries. We are cooperating with industry and state research horticulturists in the introduction of improved varieties of Northwest soft fruits and berries. Improved cultural practices and preservation methods are under study. Evaluation of raspberry hybrids led to the introduction of Meeker, a high yielding, new variety that tolerates freezing very well. It has good red color and fine flavor, but large seeds. Over half of the 46 strawberry and 84 raspberry hybrid selections evaluated as frozen fruit have been eliminated because they were of poor quality

when processed. Strawberries, raspberries, cherries and sliced Elberta peaches frozen by immersion in Freon 12 had better texture than air-blast frozen fruit. Texture of Freon-frozen peach slices after thawing in syrup was similar to fresh peach texture. Thawed slices stored at 35° F. in syrup containing 1% ascorbic acid and 0.1% potassium sorbate retained good eating quality for 2 months. Drained weight of canned blueberries, as well as the viscosity and pectin content of the syrup in which they were packed, were influenced by harvest intervals.

4. Fluidized-bed Freeze Drying of Fruit and Fruit Powders. Malecki Laboratories, Inc., Chicago, Illinois, is conducting contract research to develop a continuous fluidized-bed freeze dryer for making fruit juice powders. The apparatus has been erected. Fruit juice is sprayed into the chamber by a rotating disk. A stream of liquid nitrogen enters through a perforated ring around the top of the chamber and runs down the walls of the chamber to cool it. A thin section collects the frozen droplets and acts as a fluidized bed, once sufficient droplets have collected. Air can be admitted into the bottom of this thinner section to fluidize the particles lying above. The apparatus will have low capacity but will demonstrate process principles.

5. Dried Fruit and Dried Fruit Products. Research is conducted to develop new products and improved processes to increase markets for dried fruits. Air-packed and nitrogen-packed Winesap applesauce flakes with good initial quality remained nearly unchanged in flavor after one year at room temperature, but color darkened slightly in the air-packed sample. Samples with marginal initial quality needed the protection of nitrogen packing. Can fill weight (bulk density) was doubled by hot-rolling dried applesauce flakes into a dense sheet and regrinding it into granules which still reconstitute instantly. Instant applesauce is about 33% cheaper to produce by drum drying than by the process that starts with evaporated apples, and the densified drum dried instant applesauce meets military specifications.

6. Process Modification to Reduce or Find Uses for Food Processing Wastes. To help minimize pollution of land, waters and atmosphere from sources associated with food processing, we have initiated exploratory studies on disposal or reclaiming of food processing wastes.

PUBLICATIONS -- USDA AND COOPERATIVE PROGRAMS

Chemical Composition and Physical Properties

- Bennett, Raymond and Heftmann, Erich. 1966. Biosynthesis of pregnenolone from cholesterol in haplopappus heterophyllus. *Phytochem.* 5:747-54.
- Bennett, Raymond D., Ko, Shui-Tze, and Heftmann, Erich. 1966. Effect of photoperiodic floral induction on the metabolism of a gibberellin precursor, (-)-kaurene, in *pharbitis nil*. *Plant Physiol.* 41(8):1360-3.
- Bennett, Raymond D., Heftmann, Erich, and Ko, Shui-Tze. 1966. In vivo conversion of a steroidal alkaloid, holaphyllamine, to pregnenolone. *Phytochem.* 5:517-21.
- Bennett, Raymond D., Lieber, Ellen Ruth, and Heftmann, Erich. 1967. Biosynthesis of Neotigogenin and 16 -5 α -pregnen-3 β -ol-20-one from cholesterol in *Lycopersicon pimpinellifolium*. *Phytochem.* 6(6):837-40.
- Cleland, Robert and Olson, Alfred C. 1967. Metabolism of free hydroxyproline in *Avena coleoptiles*. *Biochem.* 6(1):32-6.
- De Jong, Donald W. 1967. An investigation of the role of plant peroxidase in cell wall development by the histochemical method. *J. Histochem. Cytochem.* 15(6):335-46.
- De Jong, D. W., Olson, A. C., Jansen, E. F. 1967. Glutaraldehyde activation of nuclear acid phosphatase in cultured plant cells. *Science* 155(3770):1672-74.
- Heftmann, Erich. 1966. Chromatography. In "Encyclopedia of Chemistry," 2nd ed., G. L. Clark, ed., Reinhold, N. Y. pp. 236-8.
- Heftmann, Erich, Ko, Shui-Tze, and Bennett, Raymond D. 1966. Identification of estrone in pomegranate seeds. *Phytochem.* 5(6):1337-9.
- Heftmann, Erich, Lieber, Ellen Ruth and Bennett, Raymond D. 1967. Biosynthesis of tomatidine from cholesterol in *Lycopersicon pimpinellifolium*. *Phytochem.* 6(2):225-29.
- Olson, A. C., Hawker, K. M., De Jong, D. W., and Jansen, E. F. 1967. Alteration of acid phosphatase, peroxidase and malate dehydrogenase isozymes in a plant tissue culture. *Fed. Amer. Soc. Expt. Biol.* 26(2):835.
- Pharis, Richard P., Ruddat, Manfred, Phillips, Cornell and Heftmann, Erich. 1967. Response of conifers to growth retardants. *Bot. Gaz.* 128(2):105-109.

- Sauer, Horst H., Bennett, Raymond D. and Heftmann, Erich. 1967. Conversion of pregenolone to digifoligenin by *Digitalis lanata*. Sonderdruck aus der Zeitschrift Die 54(9):226-27.
- Schwimmer, Sigmund and Olivera, Baldomero M. 1966. Electrophoretic properties of enzymically synthesized DNA. J. Molecular Biol. 20:585-7.
- Schwimmer, Sigmund. 1966. DNA polymerase activity of mung bean seedlings. Phytochem. 5(4):791-4.
- Schwimmer, Sigmund and Aronson, A. K. 1966. Apparent synthesis of single-stranded DNA by DNA polymerase at high template concentrations. Life Sciences 5(15):1415-22.
- Schwimmer, Sigmund and Olivera Baldomero M. 1966. Electrophoresis of products of DNA- and nucleohistone-supported DNA synthesis. Biopolymers 4(8):953-5.
- Schwimmer, Sigmund and Aronson, Arlene. 1967. Susceptibility to nucleases of DNA synthesized with nucleohistone primer. Biochim. Biophys. Acta. 134(1):59-68.

Flavor

- Flath, R. A. 1967. New techniques in fruit volatiles research. Agr. Sci. Review 5(1):27-32.
- Flath, R. A., Black, D. R., Guadagni, D. G., McFadden, W. H. and Schultz, T. H. 1967. Identification and organoleptic evaluation of compounds in delicious apple essence. J. Agr. Food Chem. 15(1):29-35.
- Flath, R. A., Henderson, N., Lundin, R. E. and Teranishi, R. 1967. Microcell for nuclear magnetic resonance analyses. Appl Spectroscopy 21(3):183-4.
- Guadagni, D. G. and Harris, Jean. 1967. Stability of frozen concentrated apple juice with and without added essence. Food Technol. 21(3A):136-38.
- Guadagni, D. G., Okano, S. and Harris, Jean. 1967. Effect of temperature on storage stability of apple essence obtained from different varieties. Food Technol. 21(4):179-82.
- McFadden, W. H. 1966. Introduction of gas-chromatographic samples to a mass spectrometer. Separation Science 1(6):723-46.

- Schultz, T. H., Flath, R. A., Black, D. R., Guadagni, D. G., Schultz, W. G., and Teranishi, R. 1967. Volatiles from delicious apple essence--extraction methods. *J. Food Sci.* 32(3):279-283.
- Stevens, K. L., Bomben, J. L. and McFadden, W. H. 1967. *J. Agr. Food Chem.* 15(3):378-80.
- Teranishi, Roy. 1966. Advances in fruit flavor chemistry. In "Flavor Chemistry," American Chemical Society Advances in Chemistry Series 56:121-30, Washington, D.C.
- Teranishi, Roy, Lundin, R. E., McFadden, W. H., Mon, T. R., Schultz, T. H., Stevens, K. L., and Wasserman, Jan. 1966. Orange compounds. Volatiles from oranges. Oxygenated compounds identified by infrared, proton magnetic resonance, and mass spectra. *J. Agr. Food Chem.* 14(5):447-9.
- Teranishi, Roy. 1967. High resolution gas chromatography in aroma research. *Perfumery & Essential Oil Record* 58(3):172-78.
- Teranishi, Roy, Lundin, R. E. and Scherer, J. R. 1967. Analytical technique. In "Chemistry and Physiology of Flavors," pp. 161-81, Avi Publishing Co., Westport, Conn.
- Webb, A. Dinsmoor, Kepner, Richard E., and Maggiora, Linda. 1966. Gas chromatographic comparison of volatile aroma materials extracted from eight different muscat-flavored varieties of *vitis vinifera*. *American Journal of Enology and Viticulture* 17(4):247-254. (Contract)

Color, Texture and Other Quality Factors

- Asen, Sam and Jurd, Leonard. 1967. The constitution of a crystalline, blue cornflower pigment. *Phytochem.* 6(4):577-84.
- Chakravarty, D., Dutta, S. P., and Mitra, A. K. 1966. Modified method for the synthesis of 3-amino coumarin. *Cur. Sci.* 34(6):177-9. 1/
- Corse, Joseph, Lundin, R. E., Sondheimer, Ernest, and Waiss, A. C., Jr. 1966. Conformation analyses of D-(-)-quinic acid and some of its derivatives by nuclear magnetic resonance. *Phytochem.* 5(4):767-76.
- Curl, A. Laurence. 1966. The carotenoids of muskmelons. *J. Food Sci.* 31(5):759-61.
- Gaffield, W., Waiss, A. C., Jr., and Corse, J. 1966. Conformational studies of quinic acid and some derivatives. *J. Chem. Soc. Part C* 20:1885-7.

1/ Research supported by P.L. 480 funds.

- Harel, E., Mayer, A. M., and Shain, Y. 1966. Catechol oxidases, endogenous substrates and browning in developing apples. J. Sci. Food Agr. 17:389-92. 1/
- Jurd, L. 1966. Methods of using flavylum compounds for food coloring. U. S. Patent No. 3,266,903.
- Jurd, L. 1966. Anthocyanidins and related compounds--X. Peroxide oxidation products of 3-alkylflavylum salts. Tetrahedron 22(8):2913-21.
- Jurd, L. 1967. Anthocyanidins and related compounds XI. Catechin-flavylum salt condensation reactions. Tetrahedron 23(3):1057-64.
- Jurd, Leonard, Waiss, A. C., and Bergot, B. J. 1965. Condensation reactions of flavylum salts. Bul. Natl. Sci. India No. 31:69-77.
- Jurd, Leonard and Asen, Sam. 1966. The formation of metal and "co-pigment" complexes of cyanidin 3-glucoside. Phytochem. 5(6):1263-71.
- Jurd, Leonard. 1966. Anthocyanin-copigment complexes. Wines & Vines 47(7):22.
- Jurd, Leonard. 1966. Quinone oxidation of flavenes and flavan-3,4-diols. Chem. and Indus. 40:1683-4.
- Jurd, Leonard. 1967. Flavylum compounds and methods of using them. U.S. Patent No. 3,314,975.
- Jurd, Leonard. 1967. Acidic fruit and vegetable food and method of coloring employing benzopyrylium compounds. U.S. Patent No. 3,301,683.
- Mayer, A. M., Harel, E., and Ben-Shaul, R. 1966. Assay of catechol oxidase - A critical comparison of methods. Phytochem. 5:783-9. 1/
- Miura, Hiroshi, Kawano, Nobuske, and Waiss, Anthony C., Jr. 1966. Cryptomerin A and B, Hinokiflavone methyl ethers from the leaves of Cryptomeria japonica. Chem. & Pharm. Bul. 14(12):1404-1408.
- Waiss, A. C., Jr., Kuhnle, J. A., Windle, J. J., and Wiersema, A. K. 1966. Oxidative condensation of catechols and resorcinols. Tetrahedron Letters No. 50:6251-5.

Microbiology and Toxicology

- Popper, K. and Nury, F. 1966. DEPC sterilization of cold storage rooms. ASHRAE J. 8(8):80-1.

Thomas, John O., Riebelin, William E., Wilson, Robert H., Keppler, Douglas C., and DeEds, Floyd. 1967. Chronic toxicity of diphenylamine to albino rats. *Toxicology and Applied Pharmacology* 10, 362-374.

Technology--Process and Product Development

Bolin, H. R. and Nury, F. S. 1967. Dried fruit uses enhanced by new method of gelling. *Canner/Packer* (West. ed) 136(5):39.

Bomben, John L., Kitson, John A., and Morgan, A. I., Jr. 1966. Vacuum stripping of aromas. *Food Technol.* 20(9):125-8.

Boyle, Frank P. 1966. Work at the Western Regional Laboratory. In "Processing and Expanding Apple Crop, Proceedings Report of the National Apple Industry Utilization Conference," D. G. Dalrymple and B. A. Twigg, eds., Univ. of Maryland, pp. 61-4.

Boyle, Frank P. 1966. Osmovac drying of apples. In "Processing an Expanding Apple Crop, Proceedings Report of the National Apple Industry Utilization Conference," D. G. Dalrymple and B. A. Twigg, eds., Univ. of Maryland, pp. 103-6.

Ingalsbe, D. W. and Neubert, A. M. 1966. Colloid stability of frozen concentrated apple juice. *Wash. State Hort. Assoc. Proc.* 62:139-144.

LaBelle, R. L. 1966. Characterization of foams for foam-mat drying. *Food Technol.* 20(8):89-94.

Lazar, M. E. and Morgan, A. I., Jr. 1966. Instant applesauce. *Food Technol.* 20(4):179-82.

Lee, C. Y., Salunkhe, D. K., and Nury, F. S. 1966. Effects of dehydration processes on flavor compounds and histology of apricots (Prunus armeniaca). *J. Sci. Food Agr.* 17(9):393-5.

Lee, C. Y., Salunkhe, D. K., and Nury, F. S. 1967. Some chemical and histological changes in dehydrated apple. *J. Sci. Food Agr.* 18(3):89-93.

Malecki, Geo. J. 1967. Freeze-drying process and apparatus. U.S. Patent No. 3,313,032.

Morgan, A. I., Jr. 1966. Foam-mat drying. *ASHRAE J.* 8(11):58-9.

Neubert, A. M. and Ingalsbe, D. W. 1966. Characteristics of apple juice from commercial rack-and-cloth presses. *Proc. Wash. State Hort. Assoc.* 62:135-38.

Ponting, J. D., Watters, G. G., Forrey, R. R., Jackson, R., and Stanley, W. L. 1966. Osmotic dehydration of fruits. *Food Technol.* 20(10):125-8.

- Popper, K., Camirand, W. M., Stanley, W. L., and Nury, F. S. 1966. Osmotic emergency purifier of sea water. *Nature* 211(5046):297-8.
- Popper, K., Camirand, W. M., Watters, G. G., Bouthilet, R. J., and Boyle, F. P. 1967. Recycles process brine prevents pollution. *Food Engin.* 39(4):78-80.
- Salunkhe, D. K., Lee, C. Y., and Nury, F. S. 1966. Maintaining quality in processed fruit. *Utah Farm and Home Sci.* 27(3):104-7.
- Strashun, S. I. and Talburt, W. F. 1966. Continuous dehydration of edible liquids. U.S. Patent No. 3,241,981.
- Wolford, Everett. 1967. Observations on the Meeker raspberry for freezing and preserving. *Western Wash. Hort. Proc.*

AREA NO. 8. POTATO UTILIZATION - FOOD

Problem. The potato industry, faced with a continuing decline in the consumption of fresh potatoes, is becoming more and more dependent upon the development of new and improved processed products to maintain markets and to avoid recurring economic disasters. Crop perishability, supply fluctuations, and the inelasticity of demand result in wide swings in price with even slight surpluses. In producing areas having a substantial processing industry, growers can moderate depressive lows by contracting with processors prior to harvest. However, in many important potato growing areas where processing has not yet developed, growers are still vulnerable and the situation is exaggerated by the mounting competition from processed potato and other food products. A continuing improvement in processed potato products is clearly required if processing is to expand fast enough to offset the progressive decline in use of fresh potatoes.

To improve the quality of processed potatoes, ways must be found to eliminate the stale, earthy, rancid, green, and warmed-over flavors that are sometimes encountered in potato products, including dehydrated mashed potatoes, dehydrated diced potatoes, frozen french fried, frozen patties, and potato chips, and to retain the desirable natural flavor of freshly cooked potato. Research methods recently developed offer an opportunity to isolate and identify the constituents responsible for the natural flavors and the off-flavors, to develop rapid and sensitive analytical methods for their measurement, and to determine the raw material factors controlling formation of the various desirable and undesirable constituents in the fresh potato.

Further improvement in the texture of potato products is also needed. Fundamental histological and chemical investigations could reveal the causes of differences in the texture of potatoes, as a basis for developing improved processing methods.

Enzymes play a great part in the entire compositional pattern of the potato, not only the constituents responsible for flavor, off-flavor, color, and texture, but also those responsible for disorders such as black spot. Black spot causes severe losses, both to those who market potatoes fresh and to those who process potatoes, because trimming costs are sharply increased and yields reduced. Increased knowledge of enzymes is needed as a basis for solving the black spot and similar problems, for increasing use of potatoes by reducing costs, and for improving quality of both fresh and processed potatoes.

Perhaps the most urgent problem presently facing the potato processing industry is the disposal of plant wastes. Establishment of new strict standards for the discharge of plant effluents into lakes and streams will require research in three areas: the effects of modified plant

operations on the volume and nature of wastes, ways of recovering useful fractions from the wastes, and ways of treating the remaining effluent to lower the BOD (biochemical oxygen demand) to an acceptable level,

USDA AND COOPERATIVE PROGRAMS

In the Western Utilization Research and Development Division, basic and applied research on potato products is conducted at the Division headquarters at Albany, California, and by grant funds in Davis, California and under P.L. 480 in Sweden. The chemistry of potato flavor and the compounds involved in deterioration of potato products are studied to provide a basis for new and improved potato processes and products. Histochemical studies are conducted to elucidate factors involved in the texture of potato products. Basic investigations on the enzyme systems involved in potato product discoloration and the mechanism of rancidity development are in progress.

The Federal program of research in this area totals 5.7 scientist man-years including the equivalent of 0.7 scientist man-years for a research grant. Of this number, 0.7 are assigned to chemical composition and physical properties and 5.0 to technology--process and product development. In addition, the Division sponsors two research grants under P.L. 480.

PROGRAM OF STATE EXPERIMENT STATIONS

A total of 7.5 scientist man-years is devoted to this area of research.

PROGRESS -- USDA AND COOPERATIVE PROGRAMS

A. Chemical Composition and Physical Properties

1. Enzyme Interactions. The University of Gothenburg in Sweden, supported by P.L. 480 funds, is conducting research to determine how metal ions influence enzyme catalysis, as a means to control stability of vegetable products. The enzyme 3-phosphoglycerate kinase (PGA kinase) catalyzes the transfer of phosphate from adenosine triphosphate (ATP) to 3-phosphoglycerate (PGA). Its activity requires the presence of magnesium ion. It was found that magnesium is first bound to ATP and then this complex becomes attached to the PGA kinase at an active site. The PGA is attached at a different site along the chain-like enzyme molecule. The active site in carbonic anhydrase enzyme involves a histidine residue and the sequence of amino acids at the carboxyl end of the enzyme molecule. The amino acid sequence is different for different forms (isoenzymes) of carbonic anhydrase. An active site on the carbonic anhydrase molecule will bind anions or specific sulfonamide inhibitors. The enzyme phosphatase contains zinc atoms combined at two identical sites. Zinc was found not to be essential for binding, but it does influence the binding process. The active site on the molecule of laccase contains two copper atoms bound to nitrogen atoms in the molecular chain,

The mechanism of lipid formation is being investigated under a grant made to the University of California at Davis. Information obtained under this study would be used to find ways to alter the ratio of saturated and unsaturated fatty acids in foods, select vegetables for processing, control oxidation during and after processing, and measure adequacy of blanching. In addition to potatoes, other vegetables are studied under this grant. Spinach chloroplasts contain an inhibitor of acetyl CoA carboxylase, a key enzyme of fatty acid synthesis. It combines with the enzyme and not the substrate, is heat stable, and consists of at least two molecular species. This inhibitor with its thermal stability may be of practical use as an index protein for assessing adequacy of blanching of processed vegetables.

Enhancement of fatty acid synthesis in potato discs occurs at a very early phase of "aging" and to a more pronounced extent than other changes, such as enhanced protein synthesis and respiration. Experiments with anti-biotics as probes suggest that the major cause of this enhancement is the increased synthesis of the proteins (enzymes) constituting the fatty acid synthesizing enzyme system. The increased protein synthesis seems to imply the operation of a system for derepression of the operon (complex of genes) coding for these enzymes. This work may eventually yield a clue to means to manipulate the enzymes of a given vegetable so as to enhance desirable and suppress undesirable reactions.

2. Fat autoxidation. The Swedish Institute for Food Preservation Research at Gothenburg, Sweden, is using P.L. 480 funds to study the factors affecting the rate of autoxidation of fat as a basis for the development of improved processing methods for dehydrated potatoes and other vegetables to decrease their tendency to turn rancid. In general, decreasing the concentration of oxygen in the atmosphere did not dramatically lower the rate of fat oxidation. In 1% oxygen the rate was half that in air (20% oxygen). Factors which increase the absolute rate of oxidation, such as higher temperature, stronger illumination, or higher concentration, decreased the rate of oxidation at low oxygen pressure relative to that in air. The effect of added antioxidants was found to be somewhat reinforced at low oxygen pressure due to an extension of the "induction period". Antioxidants prolong the induction period but do not decrease the post-induction rate of oxidation. However combined addition of antioxidants and certain amino acids causes both a prolongation of the induction period and about a 50% decrease in the post-induction rate of oxidation. In the presence of certain added metal ions which generally act as pro-oxidants low oxygen pressure strikingly decreased the relative rate of oxidation.

B. Technology -- Process and Product Development

1. Factors Affecting Color and Flavor Stability of Processed Potatoes. To improve the color, flavor, texture, and stability of frozen and dehydrated potatoes, we are conducting a study of raw material and processing variables. Water-holding capacity of gelled starch was reduced when frozen par-fries

were thawed and held at 45-55° F. for one to several days before finish-frying. Thawed and held fries had a drier texture and two to three times more absorbed fat than those fried immediately after thawing.

Phenoloxidase, peroxidase, and catalase activities were completely retained in freeze-dried potato tissue and in an acetone extract. Phenoloxidase and peroxidase showed no loss of activity in six months; catalase activity decreased after three months. Phenoloxidase activity in extracts from black spot-susceptible and black spot-resistant potato tissues showed no relationship to tissue discoloration when catechol, cresol, tyrosine, chlorogenic acid, and caffeic acid were used as substrates.

Gas chromatography of amino acids and organic acids in potatoes, using several volatile derivatives (silyl-proton exchange, boron trifluoride and N-methyl trifluoroacetyl esterification), is being used with ion-exchange chromatography to determine possible qualitative and quantitative associations with both enzymic and non-enzymic discoloration.

PUBLICATIONS -- USDA AND COOPERATIVE PROGRAMS

Chemical Composition and Physical Properties

- Aisen, Philip, Aasa, Roland, Malmstrom, Bo. G., and Vanngard, Tore. 1967. Bicarbonate and the binding of iron to transferrin. J. Biol. Chem. 242(10):2484-90. 1/
- Burton, David and Stumpf, Paul K. 1966. Fat metabolism in higher plants. XXXII. Control of plant acetyl-CoA carboxylase activity. Arch. Biochem. Biophys. 117(3):604-14. (Grant)
- Larsson-Raznikiewicz, Martha. 1967. Kinetic studies on the reaction catalyzed by phosphoglycerate kinase. II. The kinetic relationships between 3-phosphoglycerate, $MgATP^{2-}$ and activating metal ion. Biochim. Biophys. Acta. 132:33-40. 1/
- Lindskog, S. and Ehrenberg, A. 1967. Magnetic susceptibility and near infrared spectra of bovine cobalt carbonic anhydrase. J. Molecular Biol. 24:133-37. 1/
- Nyman, Per Olof, Strid, Lars, and Westermarck, Gunvor. 1966. Carboxyl-terminal amino acid sequences of human and bovine erythrocyte carbonic anhydrase. Biochim. Biophys. Acta. 122:554-6. 1/
- Reeve, Roger M. 1967. Starch and texture of potato products. USDA ARS-74-40, pp. 58-65.
- Willemot, Claude and Stumpf, P. K. 1967. Fat metabolism in higher plants. XXXIII. Development of fatty acid synthetase during the "aging" of storage tissue slices. Canad. Jour. Botany 45(5):579-84. (Grant)
- Willemot, Claude and Stumpf, P. K. 1967. Fat metabolism in higher plants. XXXIV. Development of fatty acid synthetase as a function of protein synthesis in aging potato tuber slices. Plant Physiol. 42(3):391-7. (Grant)

Technology--Process and Product Development

- Burr, Horace, K. 1966. Compounds contributing to flavor of potatoes and potato products. Proc. Plant Science Symposium, Campbell Soup Co., pp. 83-97.
- Huxsoll, C. C. 1967. Use of microwaves in producing large potato dice. USDA, ARS-74-40, pp. 52-58.

1/ Research supported by P.L. 480 funds.

- Reeve, R. M. 1967. Suggested improvements for microscopic measurement of cells and starch granules in fresh potatoes. Amer. Potato J. 44(2): 41-50.
- Schwimmer, Sigmund and Burr, Horace K. 1967. Structure and chemical composition of the potato tuber. Potato Handbook 12:42-5.
- Weaver, M. L. and Feinberg, B. 1967. New developments in potato processing. Wash. State Potato Conf. Proc., 6th, pp. 183-89.
- Weaver, M. L. 1967. Harvesting potatoes into water. USDA, ARS-74-40, pp. 39-42.

AREA NO. 9. VEGETABLE UTILIZATION - FOOD

Problem. Vegetable crops, in general, are perishable and seasonal and thus are subject to supply and price fluctuations to the disadvantage of the agricultural economy. In order to expand markets and stabilize prices, new and improved processed products are needed that will be desirable to the domestic and foreign consumer from the standpoint of quality, convenience, stability, nutritive value, safety, and cost. The quality of processed vegetables and the economy of their processing have not improved rapidly enough to increase or even maintain the relative position of vegetables in the American diet, or to increase substantially their contribution to the export trade. The consumption of dry beans and certain other vegetables is limited by the fact that they cause flatulence.

New easy-to-prepare vegetable products are needed, particularly from such commodities as dry beans and peas, which now require hours to prepare. The severe heating required to sterilize low-acid foods, which include most vegetables, seriously impairs the quality of canned products. The stability of all kinds of processed vegetables needs to be improved so that quality and nutritive value will be better preserved during storage and distribution. The safety and effectiveness of new chemical additives, needed to improve the quality and stability of processed vegetables, must be established. Processing operations need to be modified to cope with special problems arising from the trend toward mechanical harvesting of many vegetables. Better methods of removing residues of agricultural chemicals from vegetables for processing are urgently needed, as are procedures for decontaminating vegetables exposed to radioactive fallout. Of vital importance is research to reduce the costs of processing in order that the farmer may receive a larger share of the consumer's dollar.

Applied research on these practical problems must be supported by a strong program of basic research on the chemical constituents of vegetables responsible for flavor, color, and texture; on the reactions these compounds undergo before, during, and after processing; on constituents having biological activity; on the microscopic structure of vegetables and vegetable products; and on the micro-organisms which cause spoilage or loss of quality in these products.

USDA AND COOPERATIVE PROGRAMS

In the Western Utilization Research and Development Division, a broad program of basic research on vegetables and the application of science to new and improved products and processes is conducted at the Division headquarters at Albany, California, in field stations at Pasadena, California and Puyallup, Washington; by contracts and grants at Urbana, Illinois, East Lansing, Michigan, and Davis and Berkeley, California; and by grants under P.L. 480 in Finland, India, and France. Fundamental studies are

conducted on the chemistry of vegetable flavors and vegetable pigments, the mechanism of heat resistance in bacterial spores, the composition of dry beans as related to cooking quality and flatulence-producing characteristics, the factors affecting deterioration of dehydrated vegetables, and the microbiology of raw vegetables for processing. Applied research is conducted to develop new and improved products including high-quality concentrated and dehydrated products and products of improved convenience; to improve processing methods, including freezing; to evaluate new processing varieties; and to develop methods for removing radioactive fallout.

The Federal program of research in this area totals 30.4 scientist man-years, including five contracts and grants. Of the total, 3.5 are assigned to investigations on flavor; 2.9 on color, texture and other quality characteristics; 5.6 on microbiology and toxicology; and 18.4 on technology--process and product development. In addition, the Division sponsors three grants under Public Law 480 on basic research.

PROGRAM OF STATE EXPERIMENT STATIONS

A total of 28.7 scientist man-years is devoted to this area of research.

PROGRESS -- USDA AND COOPERATIVE PROGRAMS

A. Chemical Composition and Physical Properties

1. Protein Components of Dry Beans. P.L. 480 funds are supporting research at the Allahabad University in India to identify components and factors contributing to the overall biological value of dry beans. Phaseolus mungo, P. aconitifolius, three varieties of P. vulgaris, and five inedible, uncultivated legume seeds were studied. Each variety of seed had its own amino acid pattern, and none was complete in respect to the essential amino acids. Two acacia varieties contained an unidentified sulfur-containing amino compound. About 60% of the total nitrogen of Phaseolus seeds was in a globulin protein. All the amino acids essential for animal nutrition were found in the globulin of one vulgaris variety. Two vulgaris varieties and the mungo and aconitifolius varieties were deficient in tyrosine and tryptophane. In the latter two, methionine was absent.

B. Flavor

1. Dehydrated Vegetables of Improved Flavor. We have concluded a study of the flavor precursors and corresponding enzyme systems which produce flavors in certain vegetables, including onions, peas, and cabbage.

Studies were conducted on the problem of bitterness in onions. Apparently when onions are sliced, no bitterness develops on standing. However, if they are comminuted into fine particles and the juice expressed, a bitterness develops in the juice. A similar phenomenon is observed if onion slices are frozen and allowed to thaw. The reaction is, in part,

enzymatic since immediate heating of the onion juice or acidification to pH 3, followed by adjustment of the pH back to the normal pH of onions, prevents the development of bitterness.

Preliminary investigations of this reaction have shown that trans 1-propenyl-2-cysteine sulfoxide (the natural precursor of flavor in onion) will produce bitterness when treated with onion enzyme. Methyl, propyl, or allyl cysteine sulfoxides yield strong odors when treated with onion enzyme, but no bitterness. The cause of formation of bitterness in finely disintegrated or crushed onion, but not in slices, is still obscure. The problem is of practical importance for those who may wish to market an onion juice or frozen slices. The bitter material has been isolated from onions as a relatively non-volatile oil consisting of sulfur-containing compounds. Chromatography has separated the oil into five distinct fractions or sulfur-containing compounds, four of which are intensely bitter and possess a definite onion flavor. It is believed that previous studies of the volatiles of onion have revealed only a part of the overall flavor pattern since the new, as yet unidentified components are in some respects more reminiscent of onion taste, in spite of their bitterness, than the volatile disulfides previously isolated. The new compounds are not disulfides but probably contain oxygen in addition to sulfur. This suggests such structures as linear or cyclic thiolsulfinates or thiolsulfonates.

It has been observed that addition of cysteine in very small amounts to food products prepared from onion and other species of the genus Allium, results in a 10- to 40-fold increase in odor intensity and in the alteration of aromagrams of the volatiles. This may find application as a food additive or flavor potentiator when applied in very small quantities.

New ninhydrin-active components have been isolated from cabbage extracts by means of ion exchange chromatography. It has not been determined whether the compounds are single amino acids or peptides, but they appear to be different from anything previously isolated.

In studying flavor compounds, mass spectrometry is providing a powerful tool for identification of individual components. However, in interpreting mass spectra we need to know how various molecules are fragmented in a mass spectrometer. To learn this, known compounds are synthesized so that their fragmentation patterns can provide insight and comparison with the patterns of unknown substances. A series of 44 aliphatic thiol esters has been prepared and purified by distillation and gas chromatography. The thiol esters $R'-C(=O)-SR''$ covered a wide range of molecular weights with R' varying from C_2 to C_8 and R'' varying from C_1 to C_{13} , including branched chains. These compounds have been examined in the mass spectrometer and their breakdown patterns established. Thiol esters are believed to be present in fruits and vegetables and knowledge of their breakdown patterns should assist in their identification.

P.L. 480 funds are supporting research by Nobel laureate A. I. Virtanen at the Biochemical Institute in Helsinki, Finland, to identify minor organic components of plants that may function as precursors of enzymic or chemical reaction products which affect flavor. A new γ -glutamyl-tripeptide containing both a reduced and an oxidized sulfur has been isolated from chive. Studies of cycloallin suggest that 2-hydroxyl-propyl cysteine is its precursor, and that cycloallin itself is one of the precursors in the lachrymatory substance of onions. The characteristic differences between onion, chive and garlic are due principally to the double bond position in the cysteine sulfoxide derivatives. A gas chromatographic method has been developed for detecting benzyl cyanide, -thiocyanate, and -isothiocyanate; it is being used to study three enzyme reactions in crushed land cress seeds.

2. Flavor Components of Hops. The U.S. Brewers Association is financially supporting research conducted to identify the components of hops that affect flavor of beverages, especially beer and ale. The presence in hops of pentadec-6-en-2-one, pentadeca-6,9-dien-2-one and pentadeca-6,9,13-trien-2-one was established. These C₁₅ unsaturated ketones have potent aromas and because they transfer easily into the wort they may be important to the brewing process. Four previously unreported sesquiterpenes of hops were also isolated and identified as ylangene, beta-ylangene, probably beta-copaene, and tentatively a beta-santalene type. A careful and thorough capillary gas chromatographic (GLC) study of the oils from five American hop varieties has been made. This provides a method for identifying varietal origin of unknown samples of hops or hop concentrates.

Humulone isomers (normal, co- and ad-) isolated by countercurrent distribution were well characterized by nuclear magnetic resonance and mass, infrared and ultraviolet spectrometry. These are being used as standards in attempts to develop a rapid GLC method of analysis of the different humulone isomers in unknown mixtures. An entirely glass GLC system was necessary for consistent results. Silyl derivatives of pure humulone gave two peaks on GLC, probably corresponding to the two possible cis:trans forms.

C. Color, Texture, and Other Quality Factors

1. Controlling Consistency of Tomato Products. We have completed a study of the basic mechanisms of fouling during transfer of heat in the evaporation and heating of liquid foods. Quantitative measurements of fouling rates were obtained from a pilot plant in which stainless steel test sections were externally heated by steam while fouling liquids flowed inside. The fouling data collected under this project and its predecessor were deemed too complex in the interrelationships of the many variables to be of immediate and widespread use to the food industry. However, the data were capable of mathematical analysis. Therefore, it was thought that a much more useful product of this research would be a control scheme for

evaporators, encompassing all the collected quantitative data on fouling rates in long tube evaporators. A mathematical statement of our results showed that feed solids variations were such as to suggest a feed-forward control system manipulating feed rate. Extreme variations in feed solids concentration are quite common in commercial practice. The objective of any finish-evaporator is to produce an unvarying product solids concentration. This is most commonly done by manipulating steam temperatures. As our data showed, this procedure is self-defeating, since fouling rates increase with the temperature of the wetted surface of the heat exchanger wall. To achieve a constant product solids output, and also to minimize fouling, a feed-forward-feed-back control scheme was developed. This system would maintain a constant surface temperature despite varying evaporation demand. This control scheme was mathematically simulated on our analog computer and found to be workable. Physical testing of the control scheme was conducted using inline optical refractometers as the continuously monitoring sensing elements to measure feed, and product solids variations. The outputs from these instruments constitute the feed forward and feed back loops around a long tube evaporator, and are mathematically correlated through an analog computer to physically adjust the feed rate to the evaporator. Although this is rather a sophisticated control mechanism for the food industry at the present time, we hope it is a forerunner of things to come. This will result in a piece of automation which could dramatically reduce costs for food processors since it will increase the amount of water evaporated between cleanouts of heat exchangers.

2. Frozen Vegetables of Improved Texture. The pack of frozen vegetables in the U.S. is approximately 2 billion pounds per year with a wholesale value of about 500 million dollars. This volume represents only 2 to 4 percent of vegetables consumed in this country. The growth of the frozen vegetable pack has not measured up to earlier expectations.

We are studying the effects of processing on tissue structure, composition and enzyme activity as they relate to the texture, color and other characteristics of frozen vegetables. In air-blast freezing, -70°C . is the lowest temperature at which microscopically visible tissue damage has been detected in green beans. Appraisal panels distinguished only with difficulty texture differences between green beans frozen in a -70°C . air blast and those frozen in liquid nitrogen (LNF). No difference was detected between LNF green beans stored 1 year at 0° and those stored 1 year at -20°F . A microwave oven was used to blanch corn-on-the-cob. Heating to a center temperature of $200-207^{\circ}\text{F}$. in 4 to 6 minutes resulted in a higher degree of peroxidase inactivation than did a 12-minute blanch in steam or boiling water. The flavor of microwave-heated corn was as good as that of steam-blanching corn.

Formation of "delay off-flavor" was studied by holding commercially vined peas at 50, 63, 65 or 80°F . before freezing. Appraisal panels found

highly significant flavor differences between control samples processed with minimum delay and the samples held 2 hours at 80°, 4 hours at 63-65°, or 7-8 hours at 50° F.

Research supported in part by the National Association of Frozen Food Packers showed that green beans and strawberries frozen extremely rapidly by immersion in liquid nitrogen have better texture than those frozen more slowly by conventional methods. This was confirmed by organoleptic evaluation. The explanation appears to lie in the microscopically visible evidence of tissue damage in conventionally frozen green beans which is absent in similar material frozen in liquid nitrogen. Slow freezing causes tangential separation of cells in the outer parts of the tissue, and cell rupture in the radial direction nearer the center. The distribution of the effects appears to be related to tissue structure. If the tissue is composed of thin-walled cells, the cell walls break during freezing. If the walls are sufficiently thick and strong, they remain intact, but cells separate from each other. Of the successive steps, blanching, freezing and cooking, only the freezing actually causes such microscopically visible damage to vegetable tissues. The two forms of damage are found only in slowly frozen products. They are not found in material frozen by immersion in liquid nitrogen or by other rapid freezing techniques. Methods providing intermediate freezing rates cause intermediate amounts of damage.

Sensory appraisal panels are able to recognize the texture changes accompanying cell wall breakage. Quite small differences in amount of damage can be recognized, even though they do not produce appreciable texture differences. The crisp character of fresh vegetables such as green beans is preserved by rapid freezing, as with liquid nitrogen.

Preliminary studies on the rate of release of intact cells from cut surfaces of vegetable pieces by action of pectinase suggested that this might be a useful measure of changes which occur in the intercellular materials during cooking, and during the initial stages of freezing before much of the water has been transformed to the solid state. However, subsequent investigations revealed wide variations in the response of tissues within the maturity ranges commonly used for processing, which severely limited the utility of the method and the study was terminated.

The shear-press has been applied to the measurement of texture differences in samples of green beans which have been exposed to various processing treatments. It was found that within a single lot of material the processing treatments could be compared in terms of maximum force required or work performed to shear the samples. However, sample differences are not sufficiently characterized by the shape of the recorder tracings to describe or permit the qualitative identification of samples. Fresh and frozen beans, after cooking, have similar shear properties. The shear press is therefore not a suitable instrument to measure quantitatively the loss of crispness that is caused by freezing.

D. Microbiology and Toxicology

1. Reducing Heat Requirements to Sterilize Canned Low-Acid Foods. The remarkable heat resistance of bacterial spores is responsible for the severe heat processing required for canned vegetable products and other foods. The severe processing is responsible for serious losses in texture, flavor, and nutritional quality. The basis of heat resistance in bacterial spores remains poorly understood, but basic knowledge of spores and techniques for their investigation are developing rapidly. It is now reasonable to hope that the molecular mechanisms that endow spores with heat resistance will be understood and methods for disrupting these mechanisms may be adaptable to practical preservation problems.

Many different species and strains of spore-forming bacteria require the presence of specific chemical compounds if they are to germinate. A supersaturated solution of calcium dipicolinate was known to act as a general germinant by by-passing such strain-specific germination requirements. 4H-pyran-2,6-dicarboxylate was synthesized and its calcium chelate was found also to act as a general germinant. This heterocyclic compound generally resembles dipicolinate but has an oxygen in the ring instead of a nitrogen. For research purposes it has the advantage of being active in sub-saturated solutions. Dense solutions of chloral hydrate in water or in glycol were also found to stimulate germination of spores.

A strain of B. macerans from spoiled canned corn was found to exhibit an unusual pattern of germination specificity. The common specific germinants are ineffective, but certain plant extracts are effective. The active factors have been isolated, and identified as fructose plus adenine. Adenine has never before been found to initiate germination. These spores with their unique germination requirements may make possible experiments leading to a better understanding of the basic mechanism of spore germination.

Methods of producing good yields of spores of food-spoilage thermophilic anaerobes are being investigated under a grant made to the University of Illinois at Urbana. The ability to produce these spores in quantity would facilitate research on the heat resistance of this class of organisms. Spores of two strains of Clostridium thermosaccharolyticum contained 13.5 and 16.3% lipid that required hydrolysis for extraction. This is far above what has been found in other spores. The fatty acids contained from 14 to 18 carbon atoms; some had one double bond; and one C₁₈ acid had an OH group. The unusually high bound fatty content of Cl. thermosaccharolyticum spores may be related to their unusual dormancy, heat resistance, or "reluctance" to sporulate well.

Detailed investigation of the enzyme activities of cell-free extracts of vegetative cells grown on glucose or on pyruvate indicates substantial differences that appear to result from feedback inhibition of enzyme biosynthesis rather than from a direct repression of enzyme activity by pyruvate.

Sporulation requirements of these strains, cleaning procedures, composition, germination requirements, and heat resistance have been determined. Resistance was increased to $D_{110^{\circ}C}$ values of 37 and 46 minutes by "maturation" in water or in pH 5.7 calcium acetate at $58^{\circ}C$.

We are conducting research to determine the mechanisms in bacterial spores that stabilize them against heat and germination, to reduce heat-processing times for low-acid food products. The hypothesis that "physiological germinants" act as allosteric effectors for proteins with functions in dormancy maintenance and release could account for the bewildering variety of highly specific germinants that act on various strains of spores. The adenine-requiring strain of B. macerans and B. megaterium are useful organisms to test this hypothesis. Adenine or 2,6-diaminopurine, with fructose or ribose, induces germination of B. macerans 7X1. Adenosine or inosine are ineffective. Response varies with cation load on spores; calcium spores respond best to adenine. Dipicolinate analogs have stringent shape requirements for Ca-DPA-type germination of B. megaterium. Ca-4H-pyran-2,6-dicarboxylate is effective; Ca-4-methyl-dipicolinate is marginally effective. Ca-Isophthalate, with a low calcium association constant, is ineffective.

The National Institute of Agronomic Research in Paris, France, supported by P.L. 480 funds, is conducting research to isolate and characterize enzymes essential for spore germination. In studies of Bacillus subtilis spores, a relationship was sought between action of amino acids on spore germination and the properties of alanine dehydrogenase and leucine dehydrogenase. A procedure was designed to obtain highly purified enzymes from vegetative cell extracts. Spore germination was observed by electron microscopy. Amino acids that initiate spore germination activate the two enzymes studied. Cytological modifications visible by electron microscopy are dependent upon activity of the enzymes.

2. Controlling Microbial Contaminants in Processed Vegetables. Sources and magnitude of microbial contamination in processing frozen vegetables are being investigated and the influence of new processing methods on microbial contamination is being evaluated. Evidence is growing that use of in-plant chlorine to supplement sound sanitary practices enables freezers to meet the 50,000 count/gram specification required by some industrial customers. Vegetable samples taken from five plants showed marked reduction in total plate count in four plants, no improvement in the other. Coliform content did not parallel total plate counts. The coliform index in samples with counts of more than 250,000/gram was never over 11/gram. Aerobacter spp. were most frequently found; Escherichia coli was found in 3% of the samples. Organisms resembling the slime producer Sphaerotilus natans were recovered from samples from the plant having the highest count. Air conveying of blanched vegetables did not lead to increased counts in three plants where the system was used. In an installation where air conveying replaced a gooseneck elevator and three conveyor belts, a marked reduction in bacterial numbers resulted.

Contract research to reduce microbial contamination that arises in the processing of dehydrated vegetables has been initiated at the University of Illinois at Urbana.

E. Technology--Process and Product Evaluation

1. Dehydrated Vegetables of Improved Stability. The wholesale value of dehydrated vegetable products, exclusive of potatoes, in the United States has been estimated at about \$75-\$80 million annually, representing \$25-\$40 million in fresh vegetables used. Advantages of dehydration over freezing and canning include savings in costs of packaging, storage and transportation through weight and space reduction gained by removal of water from the products.

We are conducting research to develop chemical and technological information to improve the stability and acceptability of dehydrated vegetables. Curled and plain leaf parsleys were analyzed for total beta-carotene, total xanthophyll, all-trans beta-carotene, and the cis-isomers, neo-beta-carotene B, and neo-beta-carotene U before and after blanching, sulfiting, air drying at 66° C. and bin drying at 47° C. Sulfited samples contained approximately 15% more total beta-carotene and xanthophylls than comparable unsulfited samples. Initial blanching or dehydration of unblanched samples gives apparent increases in assay values for total beta-carotene and xanthophylls, indicating instability of the carotenoids in raw parsley held under refrigeration or in the frozen state, or incomplete recovery from the raw product. The percentage of all-trans beta-carotene in the total beta-carotene fractions ranged from 76.1-80.4 in the unblanched, undehydrated samples to 64.6-75.9 in the dehydrated samples.

Contract research concerned with compositional and structural changes relating to the mechanism of water movement and factors influencing recovery of textural qualities has been concluded at the University of California, Davis. As determined by Lee-Kramer shear press tests and taste panel evaluations, differences were found as to the degree of dehydration permissible for carrots, celery, green beans, green bell peppers, onions, and mushrooms, before there was a loss of textural quality, or lack of crispness when the vegetables were reconstituted. Both green beans and celery were found unacceptable after only partial drying to levels of 60-67% moisture. Green bell peppers were judged "acceptable" after reconstitution when dried down to 11.8% moisture. With mushrooms, onions, and carrots, loss of textural quality as judged by taste panels was reflected in lower shear press values. For mushrooms, irreversible loss of normal texture occurred at between 18 and 27% moisture, but mushrooms dehydrated to 6.3% moisture were still judged acceptable after rehydration. Onions and carrots showed loss of normal texture when dried to moisture levels of 38 and 51%, respectively, but did not show decreases in shear press values after reconstitution, until dried to moisture levels of about 22 and 34% respectively.

Several vegetables were studied under various dehydrating conditions such as lyophilization, and high, intermediate, and low temperature drying by conventional procedures. Water vapor sorption properties and cellulosic crystallinity changes were studied. For onions, rehydration was most rapid with lyophilized tissue and this was found to be related to the structural porosity of the tissue which resulted from this form of drying. At 25° and 91° C. rehydration temperature, the original fresh tissue volume was attained in 15 to 30 minutes even though the highest degree of change in cellulosic crystallinity was found in onions dehydrated by lyophilization. Thus, the effect of tissue porosity does overcome the negative effects of increased crystallinity of cellulose with regard to readiness of rehydration. Final rehydration volumes were reached much more slowly with samples subjected to the other methods of drying and were much lower than original, fresh volumes. Cellulosic crystallinity was not significantly affected by drying temperature.

In green bell peppers the greatest increase in cellulosic crystallinity occurred with lyophilization. Some differences were observed between unpeeled and peeled (cuticularized skin removed) peppers, mainly in drying rates and rates of rehydration rather than in cellulosic crystallinity. Rehydration volumes in both cases were slightly greater at 25° C. than at 91° C.

Unlike onions, freeze-drying of green bell peppers did not produce the driest product. Data on cellulosic crystallinity indicate that changes in rates of rehydration and rehydration volume, and consequently in texture, are accompanied by changes in molecular configuration of the cellulose. That crystallinity changes in green bell peppers are not great is reflected in the comparatively small changes in textural qualities.

Onions, celery, and mushrooms were selected to study effects of degree of dehydration upon metabolic activities in relation to texture loss. Although the vegetables showed differences in rates of change in metabolic activity upon dehydration, these were not clearly related to irreversible texture change. In all cases, however, loss of metabolic activity (measured in lieu of measuring death of the tissue by drying) was accompanied by irreversible texture loss. There appeared to be a correlation between decreases in permeability and changes in texture. This occurred at a certain moisture level during drying, rather than at a constant rate.

It had been hoped that results of the study would indicate the feasibility of some means of partial dehydration of certain vegetables without irreversible texture loss upon reconstitution. The results, however, were distinctly negative with respect to this particular objective. Loss of tissue turgor responsible for fresh vegetable crispness has long been known to result when the tissue is killed, as by partial or complete dehydration. The results of the study indicate even further that only slight changes resulting from dehydration preclude the possibility of reconstituting most vegetables to a textural quality even approaching

crispness. However, in some vegetables, as onion and green bell peppers, reconstitution volumes may nearly equal fresh tissue volume. This is particularly the case with their freeze-dried products, in which tissue porosity, and comparatively less shrinkage during freeze-drying, tend to preserve gross-structural conditions despite increased cellulosic crystallinity.

2. Convenience Products from Dry Legumes. Michigan State University at East Lansing is conducting contract research which will lead to the commercial scale-up of rapidly rehydrating precooked powders from dry beans, peas, and other legumes. Cooked whole pea beans, dry peas, and lentils were successfully dried to "instant" powders. With beans, a single drum dryer with applicator rolls had a capacity of 6.64 lb. solids per hour per square foot of drum surface at a sheet moisture content of 5.2%. Capacity with a double drum dryer was about the same. Pureed cooked beans and lentils could be dried only on the single drum dryer; the purees gelatinized in the trough of the double drum dryer. Pureed cooked beans were successfully dried in a horizontal co-current spray dryer. The effects of various operating variables on capacity, product moisture, and mechanical and physical properties were determined. Spray-dried powders reconstituted somewhat more easily than did drum-dried, but a taste panel could not detect any difference after reconstitution.

To improve domestic and export markets for legumes, we are studying the composition and properties of dry beans, peas, and lentils. The aim of this research is the development of products which feature convenience in use and non-flatulent characteristics. In a cooperative study with the Department of Nutritional Sciences at the University of California at Berkeley, flatus and breath gas analyses were made on human subjects.

Immature Ventura variety Lima beans caused much less flatulence in human subjects than did mature (dry) Limas. An equal weight of dry navy beans produces more than twice the flatulence caused by mature Limas. When stachyose and raffinose, found in legume seeds, are fed to human subjects in amounts corresponding to 100 grams of dry beans, breath hydrogen rises markedly but gas passed rectally does not increase. These sugars apparently account for part of the bean-produced gas. Excitement can cause increased levels of both breath hydrogen and rectal flatus. Breath methane appears unrelated to flatulence; about 30% of people have little or no breath methane, in others the level may fluctuate on a 1- to 10-day cycle.

In storage tests of dry beans, cooking time for presoaked dry Lima, Sanilac, or pinto beans at 15.5 to 16.7% moisture increases 2-1/2- to 5-fold during storage for one year at 70° F. No parallel change occurs in rate of rehydration or in three major fractions of the pectic constituents.

Our Pasadena Laboratory is also conducting research to develop improved convenience foods from legumes. A process developed for preparing quick-cooking dry Lima beans consists of intermittent vacuum treatment (Hydravac

process) for 30 to 60 minutes in a solution of inorganic salts, soaking for six hours in the same salt solution, rinsing, and drying. The process has been modified for other legumes. Cooking time for most products is 25-40 minutes. Quick-cooking frozen Lima and other beans can be prepared from dry beans by the same process except that the salt-treated products are frozen instead of dried. Cooking times range from about 10 to 15 minutes depending upon variety and processing conditions. Nutritional value of the protein in processed Lima beans is identical to that of untreated beans.

3. Evaluation of Processing Characteristics of New Pacific Northwest Vegetable Varieties. Twenty varieties of Brussels sprouts grown at the Northwest Washington Research Unit of the State Agricultural Experiment Station were evaluated for processing quality in our continuing cooperative research program. Atlanta and Tribune, the only satisfactory varieties, toughened less as they matured than did Jade Cross, the standard variety for the area, although their oblong shape was less desirable.

Various vegetables were frozen by immersion in liquid Freon 12 at -22° F. Freon freezing (FF) times were: snow peas, 20-25 seconds; green beans, 25-30 seconds; cauliflower (1 to 1.5" curds), 90 seconds; asparagus (3/8 to 5/8" diameter), 30 seconds; (5/8 to 7/8" diameter), 45 seconds; Brussels sprouts (1.5" size), 90 seconds; cob corn, 6 minutes; cut corn, 15 seconds - almost as fast as freezing in liquid nitrogen. Shattering of FF vegetables seldom occurs. Occasional lengthwise splits in asparagus and beans are not evident after the vegetables are cooked. FF vegetables are firmer than conventionally frozen vegetables, possess more snap, and more nearly resemble fresh vegetables in texture. Residual Freon 12 in vegetables ranged from 3 to 28 ppm.

4. Removing Radioactive Fallout from Vegetables During Processing. An investigation of the removal of external and internal radioactive materials from vegetables and fruits during processing is underway by contract with the National Cannery Association in Berkeley, California. Tomatoes grown in soil enriched with strontium had 40 ppm. in the skin and 10 ppm. in the juice. Pears similarly grown accumulated strontium in the peel and core much more than in the flesh. Crops grown in soil enriched with cesium showed the following: sweet corn, somewhat higher concentrations of cesium in the pericarp than in the milk; broccoli, higher in the leaf than in the head; spinach, much higher in the root than in the leaf, vein, or stem; tomato, highest in the seeds, less in the skin, least in the flesh. Growing crops were sprayed with a simulated fallout suspension-solution containing cesium-134. Edible parts were harvested and washed or otherwise treated. With spinach, a water wash removed 80% of radioactivity; a detergent wash was slightly better; water blanching was 6 times as effective as steam blanching. Results with broccoli were similar. With peaches, little cesium was found in the flesh after water rinsing and peeling with lye or by hand. An ion exchange treatment of tomato puree shows promise of reducing cesium-134 contamination to safe levels.

5. Improved Tomato Processing. We have been working cooperatively with an industry committee to develop an analytical method for testing raw tomato material to determine its potential capacity to make products of a desirable consistency. Consistency of tomato products is largely determined by the amount and quality of pectic substances. Enzyme systems exist in tomatoes that very rapidly degrade pectic substances as soon as the tissue is disrupted. Processing methods have been developed to heat tomatoes very rapidly as they are crushed in order to reduce the degrading activity of pectic enzymes. We have discovered that by crushing tomatoes in the presence of acid, the enzymes are inhibited so that we can obtain tomato juice that has not been enzymatically degraded. This observation appears quite useful for obtaining a simple reproducible method for analyzing tomatoes for processing quality. Commercial testing of the analytical procedure has taken place in 1966 and 1967. The method also promises to be useful in selection of improved varieties with regard to consistency potential.

We are also applying this new method to a process for making tomato products of controlled consistency. By adjusting the level of acidity at the time the juice is extracted, we can make a high-consistency juice, a low-consistency juice, firm tomato-juice gels, or products like catsup or sauce with intermediate consistencies. Applications were originally made for two public service patents to cover these processes. More recently three additional applications have been filed on process improvements and on a two-step process. Processors will now be able to choose the procedure best suited to their plants for the production of high consistency products. The industry has shown an extremely active interest in the processing developments. The work has been publicized through presentations at scientific meetings, seminars, publications and press releases. More than fifty companies in the U. S. and abroad have expressed an interest. Several large American processors have investigations of this new process underway in their own research departments.

PUBLICATIONS -- USDA AND COOPERATIVE PROGRAMS

Flavor

- Amoore, John E. 1966. Current status of the steric theory of odor. *Parfumerie, cosmetique savons* 9(4):153-7; 9(5):195-9; 9(6):261-4; translated from *Ann. N.Y. Acad. Sci.* 116:457-76, 1964.
- Amoore, John E. and Venstrom, Delpha. 1967. Correlations between stereochemical assessments and organoleptic analysis of odorous compounds. In "Olfaction and Taste II." Pergamon Press, Oxford.
- Amoore, J. E. 1967. Specific anosmia; a clue to the olfactory code. *Nature* 214(5093):1094-98.
- Amoore, J. E. 1967. Stereochemical theory of olfaction. In "Chemistry and Physiology of Flavors," H. W. Schultz et al., eds., pp. 119-47, Avi Publishing Company, Westport, Conn.
- Buttery, R. G., Lundin, R. E., and Ling, Louisa. 1966. Sesquiterpene hydrocarbons of hops. *Chem. & Indus.* 28:1225-6.
- Buttery, Ron G. and Ling, Louisa C. 1966. The chemical composition of the volatile oil of hops. *The Brewers Digest* 41(8):71-7.
- Buttery, Ron G. and Ling, Louisa C. 1967. Identification of hop varieties by gas chromatographic analysis of their essential oil. *Agr. and Food Chem.* 15(3):531-35.
- Buttery, Ron G., Lundin, Robert E., and Ling, Louisa. 1967. Characterization of some C₁₅ constituents of hop oil. *J. Agr. Food Chem.* 15(1):58-65.
- Buttery, Ron G. 1967. Hop flavor. In "Chemistry and Physiology of Flavors," H. W. Schultz et al., eds., Avi Publishing Company, Westport, Conn.
- Carson, J. F. and Boggs, Lois E. 1966. The synthesis and base catalyzed cyclization of (+)- and (-)-Cis-S-(1-propenyl)-L-cysteine sulfoxides. *J. Org. Chem.* 31(9):2862-4.
- Carson, John F. and Boggs, Lois E. 1967. The synthesis of (+)- and (-)-Cis-S-(β -styryl)-L-cysteine S-oxides. *J. Org. Chem.* 32(3):673-76.
- Carson, J. F. 1967. Onion flavor. In "Chemistry and Physiology of Flavors," H. W. Schultz et al., eds., Avi Publishing Company, Westport, Conn.

- Honkanen, Erkki and Karvonen, Pertti. 1966. Isolation of volatile flavour compounds from fats and oils by vacuum carbon dioxide distillation. Acta Chem. Scand. 20(9):2626-27. 1/
- Matikkala, E. J. and Virtanen, Artturi I. 1966. A new type of gamma-glutamyltripeptide, gamma-glutamyl-S-(prop-1-enyl)-cysteinyl-S-(prop-1-enyl)-cysteine sulphoxide. Suomen Kemistilehti B39, 201-202. 1/
- Ralls, Jack W., Carson, John F., Seifert, Richard M., and Burr, Horace K. 1967. Composition and flavor modification of processed peas. USDA, ARS 74-38, p. 47.
- Schwimmer, Sigmund. 1967. Development of a bitter substance in onion juice. Food Technol. 21(3):74.
- Virtanen, Artturi I. 1966. On sulphur-containing amino acids and gamma-glutamyl peptides in the bulbs and seeds of Allium species. The Botanical Magazine, Tokyo, 79(940-941):506-509. 1/

Color, Texture and Other Quality Factors

- Brown, Milford S. 1967. Texture of frozen vegetables: effect of freezing rate on green beans. J. Sci. Food Agr. 18(2):77-81.
- Carlson, R. A., Randall, J. M., Graham, R. P., and Morgan, A. I., Jr. 1967. The rotary steam-coil vacuum evaporator. Food Technol. 21(2): 90-92.
- Neumann, H. J., Shepherd, A. D., Boggs, M. M., and Harris, J. G. 1966. Frozen Chinese waterchestnuts: blanching, storage, and quality. Food Technol. 20(11):111-4.
- Rasmussen, Clyde L. and Prouty, William. 1966. An evaluation of freezing: advantages, techniques and cost factors. Bakers Weekly 212(6):37-8 (Part I); (9):23-6 (Part II); (10):24,26,27 (Part III).
- Rasmussen, Clyde L. 1967. Economics of present and future freezing methods. ASHRAE Journal 9(6):36-41.
- Reeve, R. M. and Brown, Milford S. 1966. Some structural and histochemical changes related to frozen fruits and vegetables. Cryobiol. 3(3):214-23.

Microbiology and Toxicology

- Alderton, G. 1967. Method of sterilizing. U.S. Patent No. 3,328,178.

1/ Research supported by P.L. 480 funds.

- Hermier, J. 1965. Germination of the spores of *Bacillus subtilis*. III. Demonstration of an alanine dehydrogenase and a leucine dehydrogenase in extracts of the spores. *Ann. Biol. Anim., Biochim. Biophys.* 5(4): 483-96. 1/
- Lewis, J. C. 1967. Determination of dipicolinic acid in bacterial spores by ultraviolet spectrometry of the calcium chelate. *Analyt. Biochem.* 19(2):327-37.
- Pheil, Charles G. and Ordal, Z. John. 1967. Fatty acid composition of spores of the thermophilic anaerobes. *J. Bacteriol.* 93(5):1727-8. (Grant)
- Rousseau, Micheline, Flechon, Jacques, and Hermier, Jean. 1966. Study on spore germination in *Bacillus subtilis* by means of electron microscopy. *Annales de l'Institut Pasteur Tome* 111(2):149-60. 1/
- Snell, Neva. 1966. Heat resistance of bacterial spores. *Bay Area Biologists Society Quarterly* IV(1):1-2.

Technology--Process and Product Development

- Burr, Horace K. and Kon, Samuel. 1967. Factors influencing the cooking rate of stored dry beans. *USDA, ARS-74-41*, pp. 50-52.
- Feinberg, Bernard. 1966. Mushrooms: wild and tame. *Food Technol.* 20(9): 60-8.
- Gee, Mildred, Graham, Robert P., and Morgan, A. I., Jr. 1967. Storage changes in the free amino acids of foam-mat dried tomato powders. *J. Food Sci.* 32(1):78-80.
- Miers, J. C., Wagner, J. R., Sanshuck, D. W. 1967. Consistency of tomato products. II. Effect of pH during extraction on tomato juice consistency. *Food Technol.* 21(6):117-120.
- Morgan, A. I., Jr. 1966. Some concepts in evaporation and their origins. *Internatl. Cong. of Food Science Proc.*, 2nd, Warsaw, Poland.
- Murphy, Edwin L. 1967. The measurement of human flatulence. *USDA, ARS-74-41*, pp. 71-74.
- Olson, Robert L. 1966. Prepared frozen foods. *ASHRAE Journal* 8(7):56-7.
- Rasmussen, Clyde L., Rogers, Robert O., and Michener, H. D. 1966. Processing--A prime protector. In "Protecting Our Food," U.S. Dept. of Agr., *Yearbook of Agriculture*, pp. 153-69.

1/ Research supported by P.L. 480 funds.

- Rockland, L. B. 1966. WURDD develops quick-cooking dry beans. Food Processing/Marketing 27(9):107.
- Rockland, Louis B. and Metzler, Eugene A. 1967. Quick-cooking Lima and other dry beans. Food Technol. 21(3A):26-30.
- Rockland, Louis B. 1967. New quick-cooking dry Lima beans. USDA, ARS-74-41, pp. 16-23.
- Rockland, L. B., Hayes, R. J., Metzler, E., and Binder, L. J. 1967. Process for producing quick-cooking legumes. U.S. Patent No. 3,318,708.
- Sanchez, Roland, Tucker, Carl, and Murphy, E. L. 1967. The development of the flatulence principle in the maturing bean. USDA, ARS-74-41, pp. 53-56.
- Steggerda, F. R. and Dimmick, J. F. 1966. Effects of bean diets on concentration of carbon dioxide in flatus. Amer. J. Clin. Nutr. 19(2):120-4. (Contract)
- Wagner, Joseph R. and Miers, Jackson C. 1967. Consistency of tomato products. I. The effects of tomato enzyme inhibition by additives. Food Technol. 21(6):114-17.

AREA NO. 10. SAFFLOWER, CASTOR, AND OTHER WESTERN
OILSEEDS UTILIZATION - FOOD

Problem. Cash crops for diversification and rotation programs need to be increased, particularly in cotton-producing areas of the western states. A crop with potential for these programs is safflower, which is emerging as an important source of edible and industrial oil as well as edible seed meal for both food and feed use. Basic information is needed on the composition of the oil and meal and, to obtain this information, adequate analytical methodology must be developed. Rapid and accurate analytical methods are also needed to control and improve the processing of oil and meal.

The high percentage of linoleic acid (essential fatty acid) in safflower oil is a feature that is leading to its rapidly expanding use as a food oil. And breeding research is producing varieties with other advantages. One new variety is very high in oleic acid, providing an oil of unusual stability against oxidation in food products and in cooking. New thin-hulled varieties give greater yields of oil and seed meal, but flavor and color problems exist in the most promising thin-hulled varieties so far developed. Utilization research is required to remove the odoriferous substances and pigments so that a light-colored bland oil is obtained.

Safflower has become a significant item of export, with 240,000 tons of safflower seed exported in calendar year 1964. This export was essentially all to hard-currency customers, so it benefits our unfavorable international trade balance. Competition from Russian sunflower has developed last year so that research is needed to strengthen the position of safflower by improving the value of its products.

Castor also can provide the diversification that is needed in western growing areas. But we anticipate only limited food use of it, although the oil has been used in Asia for centuries for cooking purposes.

Basic and applied research is needed to provide improved processes for and products from safflower, castor, and other western oilseeds.

USDA AND COOPERATIVE PROGRAMS

In the Western Utilization Research and Development Division, both basic and applied research are conducted on safflower and castor seed at the Division headquarters at Albany, California and under contract at Tucson, Arizona. Basic compositional studies on oilseed meals are concerned with the resolution of their water-soluble proteins and determination of their nutrient properties for food. Studies are conducted on the composition and stabilities of safflower oils. New analytical techniques also are being developed.

The Federal program of research in this area totals 5.4 scientist man-years (including contract research) assigned to research on technology -- process and product development.

PROGRAM OF STATE EXPERIMENT STATIONS

A total of 2.4 scientist man-years is devoted to research on food uses of other oilseed crops, including safflower.

PROGRESS -- USDA AND COOPERATIVE PROGRAMS

A. Technology -- Process and Product Development

1. Development of Highly Stable Safflower Oils. The University of Arizona in Tucson is conducting contract research to identify antioxidants and antioxidant systems in high-stability safflower oils. No correlation appears between tocopherol content and the induction period for oxidation of safflower oils. The addition of propyl gallate to safflower oil gave greater protection from oxidation than an equivalent amount of added tocopherol. A variety of oil samples were evaluated for relative stability. High-oleic safflower oil has about four times the induction period of the best high-linoleic varieties. Stability is related to low linoleic acid content. A series of unrefined safflower oils showed the same relative order of stabilities at both 37° and 50° C. Mixing more-stable and less-stable oils results in a lowering of total stability. Alkali-refined oils are considerably less stable than non-refined oils. Oil-water emulsion systems show increased rates of autoxidation. We are conducting research to improve the high-temperature stability of safflower oil by elucidating the oxidation and polymerization reactions involved in its deterioration. Volatile oxidation products from safflower oil, methyl linoleate, and 6,9-octadecadiene have been analyzed. They include hydrocarbons, aldehydes, ketones, formate esters and some heterocyclic compounds. Polymeric products from methyl linoleate include dimers containing no additional oxygen as well as dimers with up to four or five oxygen atoms introduced.

High-oleic safflower oil showed less viscosity increase, less polymer formation and less change in fatty acid constituents than ordinary safflower, soybean, cotton seed or commercial hydrogenated frying oils under the conditions of deep fat frying. It performed as well as other oils and remained liquid at low temperatures. Tests have been initiated to compare organoleptic properties of potato chips fried in high-oleic safflower oil with those of chips prepared in commercial hydrogenated oil and regular safflower oil. Early results indicate odor panel preference for the chips fried in the two safflower oils.

2. Nutritional and Useful Foods from Safflower and Other Western Oilseeds. We are conducting research to identify both the useful and deleterious components of safflower seed and meal, and to assess their effects on

the nutritional quality or palatability in foods. The bitter flavor associated with safflower meal can be extracted with ethanol, isopropanol, or acetone containing 20-30% water to yield a bland protein concentrate. Assays show that the extracted material is not metabolized by rats. The meal after extraction and with lysine supplementation is the equivalent of soy meal in available energy and feed efficiency. Laboratory-scale wet milling and elutriation have been effective in removing undesirable fiber from whole seed or meal and larger scale development of the process is underway. A simple procedure has been developed for estimation of lysine (enzymatic method), and the world collection of safflower seed is being surveyed for a high-lysine variety. Thin-hulled, brown-stripe safflower seed yields more oil than commercial seed, but the oil has undesirable odor and color. The odor comes from the hulls and includes alcohols, aldehydes and low-molecular weight fatty acids. Hull oil has been fractionated according to polarity. Saponification of deodorized fractions yields fatty acids with unpleasant odors. Gas chromatograms differentiate brown-stripe from commercial oil. The brown pigment of brown-stripe hulls is an insoluble melanine. Precursors to these melanines, probably phenolic materials, may be extracted with the oil from the kernel. A colorless precursor has been found in unextracted safflower and sunflower oils which forms a pigment on heating to temperatures above 130° C. Methods have been devised to prevent the extraction of this pigment precursor into the oils. Also, a method has been found by which color precursor may be removed from oils containing it.

PUBLICATIONS -- USDA AND COOPERATIVE PROGRAMS

Technology--Process and Product Development

- Fuller, G., Kohler, G. O., and Applewhite, T. H. 1966. High oleic acid safflower oil: a new stable edible oil. J. Amer. Oil Chem. Soc. 43(7): 477-8.
- Fuller, G., Diamond, M. J., and Applewhite, T. H. 1967. High-oleic safflower oil stability and chemical modification. J. Amer. Oil Chem. Soc. 44(4):264-66.
- Kohler, G. O. 1966. Safflower, a potential source of protein for human food. In "World Protein Resources," American Chemical Society Advances in Chemistry Series 57:243-53, Washington, D.C.

AREA NO. 11. SAFFLOWER, CASTOR, AND OTHER WESTERN
OILSEEDS UTILIZATION - FEED

Problem. Cash crops for diversification and rotation programs need to be increased, particularly in cotton-producing areas of the western states. A crop with potential for these programs is safflower, which is emerging as an important source of seed meal having great possibilities for food and feed use, in addition to its importance as a source of edible and industrial oil. Basic information is needed on the composition of meals and oil, and this in turn requires development of adequate analytical methodology. Rapid and accurate analytical methods are also needed to control and improve the processing of meals and oils for feed and other uses. Thin-hulled varieties of safflower, being developed through breeding research, will provide greater yields of seed meal and oil. We are cooperating with industry, state and federal plant breeders to develop analytical methodology needed to guide these studies.

Castor also can provide the diversification needed in western growing areas. Control of allergenic and toxic components of castor meal would make available a high-protein product for feed and food uses. We import much of the castor oil required for industrial use, but better utilization of domestic castor seed oil meal would increase the total value of the domestic crop and be an incentive to increase the acreage and reduce our dependence on imports. Safflower, on the other hand, has become a significant item of export with 240,000 tons of safflower seed exported in calendar year 1964. This export was essentially all to hard-currency customers, so the export of safflower and the decreased import of castor would both benefit our unfavorable international trade balance. The export of safflower has dropped in 1965 because of competition from Russian sunflower seed. A greater research effort is necessary so that safflower can improve its competitive position.

Basic and applied research is needed to provide improved processes for the products from safflower, castor and other western oilseeds.

USDA AND COOPERATIVE PROGRAMS

In the Western Utilization Research and Development Division, research on developing new and improved feeds from safflower, castor, and other western oilseeds is conducted at Albany, California. The Federal program of research in this area is equivalent to about 4.7 scientist man-years per year.

PROGRAM OF STATE EXPERIMENT STATIONS

A total of 1.5 scientist man-years is devoted to research on industrial and feed uses of other oilseed crops, including safflower.

PROGRESS -- USDA AND COOPERATIVE PROGRAMS

A. Technology--Process and Product Development

1. Practical Methods for Deallergenizing Castor Pomace for Feed Use. We have developed two commercially feasible procedures for the deallergenization of castor pomace. Suitably low allergen levels result when pomace with 8% added lime and three volumes of water is heated 30-60 minutes at 140° C. With steam alone, pomace must be heated two hours at 175° C. to give satisfactory results. Both processes destroy some heat-labile amino acids, but with supplementation, processed pomace serves as an excellent protein source in chick rations. Feeding trials have been started to determine the value of deallergenized meal in ruminant rations.

2. Improved Nutritional Quality of Safflower Seed and Meal for Feed Use. Information obtained on the composition of safflower seed and meal as related to their food potential is also applicable for their feed use. The bitter flavor associated with safflower meal can be extracted with ethanol, isopropanol, or acetone containing 20-30% water to yield a bland protein concentrate. Assays show that the extracted material is not metabolized by rats. The meal after extraction and, with lysine supplementation, is the equivalent of soy meal in available energy and feed efficiency.

Laboratory-scale wet milling and elutriation have been effective in removing undesirable fiber from the whole seed or meal. Larger scale development of the process is underway.

PUBLICATIONS -- USDA AND COOPERATIVE PROGRAMS

Technology--Process and Product Development

- Layton, Laurence L., Panzani, Raphael, and Corse, Joseph W. 1966. Non-diffusible allergenic contaminant isolated from samples of chlorogenic acid causing allergic reactions: pure chlorogenic acid not an allergen. J. Allergy 38(5):268-79.
- Layton, L. L. 1966. Human allergic serum transfer tests in marmosets: diminutive monkeys as substitutes for human patients and volunteers in allergen research and testing. Internatl. Arch. Allergy Appl. Immunol. 30(4):360-7.
- Layton, L. L. and Greene, F. C. 1966. Method of deallergenizing castor beans by treating with one molar ammonium hydroxide and with at least one part of water per part of castor bean material. U.S. Patent No. 3,294,776.
- Panzani, R. and Layton, L. L. 1966. Allergy to emanations of arthropods clinical and biological correlations: preliminary test of interpretation. Folia Allergologica XIII(4):249-68.
- Perlman, Frank and Layton, Laurence L. 1967. Stability and behavior of reaginic antibodies: effects of freezing, thawing, and lyophilizing on skin-sensitizing activity of reaginic sera. The Journal of Allergy 39(4):205-13.

AREA NO. 12. SAFFLOWER, CASTOR, AND OTHER WESTERN
OILSEEDS UTILIZATION - INDUSTRIAL PRODUCTS

Problem. Cash crops for diversification and rotation programs need to be increased, particularly in the cotton-producing areas of the western states. A crop with potential for these programs is safflower, which is emerging as an important source of industrial and edible oil, as well as of seed meal that may find uses in foods and feeds. Basic information is needed on the composition of the oil, and this requires development of adequate analytical methodology. Rapid and accurate analytical methods are also needed to control and improve the processing of oil for industrial applications. Safflower oil is particularly valued because of its non-yellowing qualities when used in surface coatings. Breeding research has yielded varieties of safflower with wide variation in fatty acid contents, pointing to the opportunity of growing specific crops for specific applications.

Castor also can provide the diversification that is needed in western growing areas. Utilization research is pointing the way to improved products such as lubricants and foamed polyurethane plastics. Domestic production of castor is so limited that much of our United States requirement must be imported, and large stocks are held by the government as a strategic reserve. Control of allergenic and toxic components of castor meal would make available a high-protein product for feed and food uses. Better utilization of domestic castor seed oil meal could increase the total value of the domestic crop and be an incentive to increase the acreage and thus reduce our dependence on imports. Safflower, on the other hand, has become a significant item of export with 240,000 tons of safflower seed exported in calendar year 1964. This export was essentially all to hard-currency customers, so the export of safflower and the decreased import of castor would both benefit our unfavorable international trade balance. Competition from Eastern European sunflower seed has developed making the research needs of safflower even more critical. Basic and applied research is needed to provide improved processes for and products from safflower, castor and other western oilseeds.

USDA AND COOPERATIVE PROGRAMS

In the Western Utilization Research and Development Division, both basic and applied research are conducted on castor and safflower seed at the Division headquarters at Albany, California; under contract in Tucson, Arizona, and by P.L. 480 grant funds in India. Studies are conducted on the composition of castor and safflower oils and on new products therefrom. New analytical and preparative techniques are developed.

The Federal program of research in this area totals 4.1 scientist man-years, including contract research. Of this total 2.0 are assigned to investigations

on chemical and physical investigations to improve products; and 2.1 to technology--process and product development. In addition, three grants are sponsored under P.L. 480.

PROGRAM OF STATE EXPERIMENT STATIONS

A total of 1.5 scientist man-years is devoted to research on industrial and feed uses of other oilseed crops, including safflower.

PROGRESS -- USDA AND COOPERATIVE PROGRAMS

A. Chemical and Physical Investigations to Improve Products

1. New Fatty Acid Derivatives from Castor and Safflower Oil for Industrial Uses. We are conducting research to synthesize nitrogen derivatives and related products from castor oil and evaluate them as industrial chemicals. Large laboratory-scale preparations of methyl 12-ketostereate have been improved by exclusion of air to prevent catalyst deactivation. The oxime of 12-ketosteric acid has been obtained in 86% yield. A sample of 12-ketostearonitrile has been prepared from 12-ketosteramide. Low-cost catalytic methods for reducing these compounds to amines are being explored. We are continuing to develop new gas-liquid and thin-layer chromatographic methods for monitoring these synthetic reactions.

Isolated yields of over 70% 10-hydroxydecanoic acid have been achieved from alkaline cleavage of ricinoleic acid or castor oil. We have found that the best reaction media for the cleavage are 1-octanol, 2-octanol, isooctanol and isodecanol. There was no increase in yield of 10-hydroxydecanoic acid when reducing agents such as sodium sulfite, sodium hypophosphite, stannous chloride and aluminum isopropoxide were added to the system.

B. Technology -- Process and Product Development

1. Commercially Useful Polymers Derived from Oils of Safflower, Castor and Other Western Oilseeds. Contract research is underway at the University of Arizona in Tucson to develop plastics, rubberlike products, or related material by polymerization or copolymerization of monomers derived from vegetable oils and naval stores. Vinyl tetrahydroabietate, vinyl dehydroabietate, and vinyl esters of commercial resins were copolymerized with vinyl chloride, vinyl acetate, butadiene and styreneacrylonitrile. Vinyl tetrahydroabietate and vinyl dehydroabietate gave a copolymer of low-molecular weight. Films from vinyl acetate and vinyl dehydroabietate showed poor mechanical properties. All copolymers with vinyl chloride could be molded at 160° C. into transparent somewhat brittle films. Butadiene copolymerized with vinyl dehydroabietate yielded largely insoluble polymers. Some terpolymer formulations gave strong rubbery films when epoxidized.

A new polymer of vinyl chloride and methyl 12-acryloxystearate (MAS) has shown excellent adhesive properties toward glass plates. Other 12-

acryloxystearate copolymers were rubbery and flexible. Copolymers of 12-methacryloxy-n-amyl stearate and methyl 14-acryloxyeicosanoate were similar to those of MAS. Epoxidation of the terminal double bond of vinyl undecylenate can be achieved with m-chloroperbenzoic acid.

Methods and formulations for commercially feasible continuous production of castor oil-based rigid foamed plastics have been investigated under contract with the Archer-Daniels-Midland Company, Minneapolis, Minnesota. Based on a statistical study of hand-mixed formulations, several castor oil-based foams were selected for large-scale production. The castor oil-based foams were compared with polyether foams. Castor oil formulations had lower physical strength but were less friable and had greater dimensional stability under humid aging conditions. Also, some flame-retardant foams from castor oil were stronger than those from polyether. Sprayed castor oil foams were comparable to similar polyether foams in physical properties, ease of application, and adhesion, but flame-retardance ratings were lower than expected. Excellent froth formulations were obtained using Freon-12 as part of the blowing agent; and shrinkage problems were eliminated. Spray, poured panel, and cut slab formulations are being evaluated under simulated use conditions.

We have initiated a research project to evaluate the utility of urethane polymers from castor oil derivatives as sealants, elastomers, and other solid or cellular plastics.

We have concluded research on a project devoted chiefly to improving the performance and reducing the cost of fluorocarbon-blown rigid urethane foams based on castor oil. Rigid foams with excellent properties were prepared from polyisocyanates and highly hydroxylated castor oil derivatives. Lower cost foams with good strength and insulating properties were developed using mixtures of unmodified castor oil and low molecular weight polyols. The process for making these foams has been licensed by one foam producer, and other concerns have evaluated the foams.

In addition to the foams discussed above, strong rigid foams, utilizing less of the expensive isocyanate component, were prepared by using blown (air oxidized) castor oil.

It was shown that the undesirable increase of thermal conductivity on aging of cut urethane foams is due to diffusion of air into the foam cells at the cut surfaces. Moreover, uncut castor oil-based foams (representative of actual foamed-in-place use) maintain their low initial thermal conductivity as well as do competitive petrochemical-based foams. No evidence of attack by fungi and other microorganisms was found in castor oil-based rigid foams, after 13 months burial in moist earth.

The future growth of rigid foam production depends to a great extent on acceptance by the building industry. Low-cost, flame-resistant foams are

required for this use. Castor oil-based foams have been made flame-resistant, with no loss in physical properties, by incorporation of 10-15% of various hydroxylated phosphorus or halogen-containing flame retardants.

Flame-resistant foams with improved properties, particularly lower shrinkage, have been prepared from crude polyisocyanates and various halogenated castor oil derivatives such as brominated, chlorinated, hypobrominated and hypochlorinated castor oils. Brominated castor oil, the most useful of these derivatives, deteriorates slowly on storage. Suitable means for stabilizing this compound have been investigated.

Particularly interesting flame-resistant foams were prepared from polyisocyanates and adducts of castor oil with perchlorocyclopentadiene. These foams have excellent physical properties and shrink much less after foaming than do comparable foams from unmodified castor oil. These adducts are considerably more stable during storage than simple halogenated castor oils.

Significant kinetic data were obtained while investigating the best conditions for formation of adducts of perhalocyclopentadienes with unsaturated fatty acid derivatives. From the effects of the location of the double bond in the chain, the configuration of the double bond, the presence of a homoallylic hydroxyl group (ricinoleate esters) and whether a perchloro- or perbromo-diene was used, it was concluded that steric factors have a pronounced effect on the rate of reaction of these heavily substituted dienes.

Supported by P.L. 480 funds, the Regional Research Laboratory in Hyderabad, India is conducting research to develop derivatives of safflower oil that will be useful in the manufacture of industrial products. Sulfation, epoxidation, and autoxidation have been studied as promising routes for the introduction of monohydroxy function into safflower oil. A critical study of reaction conditions indicates 78% sulfuric acid at 0°-25° C. and an oil:acid ratio of 1:5 of 1:10 to be optimum, but products have relatively low hydroxy values. Studies with methyl oleate and methyl linoleate indicate the reaction is selective for oleic acid residues and is therefore of little value for hydroxylating safflower oil. Controlled hydroxylation of safflower oil can be achieved by partial epoxidation followed by ring opening by selective hydrogenation after protecting olefinic double bonds with silver. Most recent studies suggest zinc may work as well as the more expensive silver in protecting the double bonds. Autoxidation of safflower oil by aeration under ultraviolet irradiation and subsequent reduction of the hydroperoxides by several techniques lead to products of about 40% hydroxylation. Attempts to increase hydroxylation by repeated oxidation reduction steps yielded dark-colored, viscous products.

The Shri Ram Institute for Industrial Research in New Delhi, India, also supported by P.L. 480 funds, is conducting research to prepare and characterize triacylated monoglycerides of ricinoleic acid and evaluate them as plasticizers. Castor oil monoglycerides of 95-96% purity have been

obtained by counter current liquid-liquid extraction using aqueous alcohol/hexane. Purification by column chromatography was not promising. Liquid-liquid extraction of pure triricinolein, while possible, does not appear practical. Synthesis of glycerol monoricinolein by direct inter-esterification of methyl ricinoleate with isopropylidene-glycerol led to disappointingly low yields; however, the reaction goes smoothly when the free hydroxyl of methyl ricinoleate is first acetylated.

A third research project supported by P.L. 480 funds is conducted at the Regional Research Laboratory in Hyderabad, India. The objective of this study is to prepare intermediates from castor oil hydroxy unsaturated fatty acids that would be useful in making polymers, protective coatings, adhesives and other products. Methodology has been developed, and more than 20 purified monomers have been prepared, characterized and submitted for evaluation.

PUBLICATIONS -- USDA AND COOPERATIVE PROGRAMS

Chemical and Physical Investigations to Improve Products

- Applewhite, T. H. and Nelson, J. S. 1966. Preparation of amides. U.S. Patent No. 3,264,281.
- Applewhite, T. H., Goldblatt, L. A., and Lundin, R. E. 1966. 12-Chloro-cis-9-octadecenyl chloride. J. Org. Chem. 31(10):3407-9.
- Applewhite, T. H., Binder, R. G., and Gaffield, William. 1967. Optical rotatory dispersion and absolute configuration of some long-chain hydroxy acids. J. Org. Chem. 32(4):1173-78.
- Freedman, Bernard, Binder, R. G., and Applewhite, T. H. 1966. Saturated keto esters from lesquerolic, dimorphecolic, and densipolic acids. J. Amer. Oil Chem. Soc. 43(7):458-60.
- Freedman, Bernard. 1967. Gas-liquid chromatography of hydroxy fatty esters: comparison of trifluoroacetyl and trimethylsilyl derivatives. J. Amer. Oil Chem. Soc. 44(2):113-16.
- Nelson, Jane S. and Applewhite, Thomas H. 1966. Castor-based derivatives: synthesis of some acrylate esters. J. Amer. Oil Chem. Soc. 43(9):542-5.

Technology--Process and Product Development

- Chandran, D. V. and Bhatnagar, R. K. 1966. A literature survey on mono-glycerides. Indian Chemical Journal 1(1):66-72. 1/
- Liepins, R. and Marvel, C. S. 1966. Polymers from vinyl esters of per-hydrogenated rosin. J. Polymer Sci., Part A-1, 4:2003-14. (Contract)
- Lyon, C. K. and Applewhite, T. H. 1967. Castor oil-based, flame resistant, rigid urethane foams. J. Cell. Plastics 3(2):91-5.
- Magin, Ralph W. and Nunnamaker, Harry G. 1966. Improved method of polymer purification. J. Polymer Sci., Part A-1, 4:2328-9. (Contract)
- Neufeld, C. H. H. and Marvel, C. S. 1966. The use of dialysis in polymer purification. J. Polymer Sci., Part A-1, 4:2907-8.
- Neufeld, C. H. H. and Marvel, C. S. 1967. Synthesis and evaluation of a series of regular polyampholytes. J. Polymer Sci., Part A-1, 5:537-43.
- Niazullah, Mohd., Chandran, D. V., Chandhok, Y. M., and Bhatnager, R. K. 1967. Acetoglycerides--their prospects and retrospects. Indian Chemical Journal (January) 1/

AREA NO. 13. POULTRY UTILIZATION - FOOD

Problem. The present technological problems in the utilization of poultry meat have grown from the profound changes in the poultry industry since World War II, which were unprecedented and are unequalled among the other agricultural industries. Per capita consumption of chicken and turkey meat has risen from 22 to 44 lbs.; the form of retail products has changed from messy uneviscerated poultry to tempting ready-to-cook or ready-to warm-and-serve items; the scale of individual commercial operations has expanded 10 to 20 fold; and vertical integration has linked breeder, hatchery, producer, and processor into vast economic aggregates. The only factor that has remained unchanged is retail price of the products, which in some cases has decreased even in the face of general wide inflationary trends. This price situation, with narrow profit margins, emphasizes the extremely competitive nature of the poultry industry. These changes have required, and will continue to demand, research to support the development of new, more efficient processes and new, more convenient and appealing products. The trend toward increased consumption of poultry should be encouraged, because poultry meat products represent a nutritious high-protein, low-fat food that is universally acceptable. Poultry is an efficient converter of feed to meat, which is low in cost relative to other meats.

The highly competitive situation in the poultry industry has accelerated further processing in order to build profits into the products. Technical problems consequent to this trend relate to the development of more efficient processing methods, retention of optimum flavor, tenderness, juiciness, and color of the products, and assurance of wholesomeness and safety. Plant processing rates of 10,000 birds per hour call for continuous automated operations, with elimination of discontinuous batch systems such as the presently required prolonged aging of birds in tanks of slush ice for adequate tenderization. Cutting the whole eviscerated birds into marketable parts has resulted in surpluses of backs and necks, which has created need for efficient methods of deboning and of utilizing the deboned meat in new products. For expanding sale of non-refrigerated products in domestic and foreign markets, there is need for improved methods of processing and maintaining quality in products that can be stored at ambient temperatures, such as dried, canned, cured, and irradiated poultry meat products.

Wholesomeness, particularly freedom from Salmonella, has become increasingly important as more poultry is processed into precooked forms that only require rewarming to serve. There is need to develop better sanitation in processing and to develop and incorporate pasteurization steps for some products so as to insure a completely safe product as the consumer receives it. To make the technological developments that can be used to build-in the values such as those mentioned, further knowledge is required on the chemical nature of poultry flavor and flavor changes during processing and storage, on

the post mortem chemical and physical changes in the poultry muscle that relate to tenderness, cohesiveness and juiciness of the meat, and on the controlled use of physical and chemical agents to pasteurize poultry meat products without seriously lowering their acceptability as foods.

USDA AND COOPERATIVE PROGRAMS

Basic and applied research on poultry meat and poultry meat products are conducted at the Division headquarters at Albany, California, and by contract in Madison, Wisconsin, Lincoln, Nebraska, and Berkeley, California. Fundamental studies on poultry flavor are concerned with the identification of flavor precursors in poultry meat and the isolation and identification of volatile flavor components developed during cooking. The chemistry of muscle protein and post mortem chemical changes are investigated relative to tenderness and other quality characteristics of poultry. The applied research is conducted on the stability of cold-tolerant microorganisms; special problems of flavor, texture and stability of precooked frozen foods; processing factors that influence tenderness of poultry meat; and maintenance of wholesomeness in poultry meat products.

The Federal program of research in this area totals 10.5 scientist man-years, including contract research. Of this number 3.5 are assigned to flavor; 3.9 to color, texture and other quality factors; and 3.1 to technology--process and product development.

PROGRAM OF STATE EXPERIMENT STATIONS

A total of 25.0 scientist man-years is devoted to research on new and improved poultry and egg products.

PROGRESS -- USDA AND COOPERATIVE PROGRAMS

A. Flavor

1. Poultry Products with Improved Flavor. Two relatively new experimental approaches have proven to be valuable in studies of the constituents and precursors of cooked poultry aroma. In one, aroma from heated tissue is concentrated by trapping in a U-tube containing absorbent at a low temperature. The volatiles are then fractionated in a gas-liquid chromatograph that permits simultaneous detection of material by flame ionization and by smelling of the fractions. Although the chromatogram is quite complex, since all products from high temperature breakdown of fats, proteins, and sugars are possible, identifications of compounds thus far completed indicate that we will be able to identify many of the reactions that occur during heating of the tissue.

A second approach consists of the fractionation by differential absorption, with solid absorbents or solutions, of aroma laden nitrogen gas and identification of the predominant aroma components by a subjective odor panel.

Fractions containing a relatively small, e.g. 6 to 8, number of components are subsequently eluted from the absorbents by heat and fractionated on a gas-liquid chromatograph. By this method of separation and subjective evaluation of the aroma components at the concentration at which they exist in the total aroma, unequivocal proof of the importance of hydrogen sulfide, ammonia or ammoniacal amines, and an unidentified but characteristic fraction has been obtained. Further, by fractionation of the potential precursors of aroma and then development of aroma from these fractions, it has been established that up to 212° F. poultry fat by itself is not a precursor of any aroma constituent. However, it performs an important function in serving as a reservoir and a blending medium for the aroma constituents developed from the other muscle constituents. The sarcoplasmic fraction of the muscle was found to contain the essential aroma precursors.

A recently initiated study is designed to determine how amines may act as synergists to antioxidants in the stabilization of fat-containing poultry meat products.

B. Color, Texture and Other Quality Factors

1. Better Quality in Poultry Meat by Control of Post Mortem Muscle Reactions.
In order to make rational technological approaches to the retention of optimum texture (tenderness, cohesiveness, and juiciness) in processed and cooked poultry meat products, it is necessary to understand what effect processing conditions have on the ultimate structural elements of the meat. Toward this end, contract studies at the American Foundation for Biological Research, Madison, Wisconsin, are underway with the objective of relating processing-induced changes in the structural elements of the muscle, observed at the electron microscopic level, with changes in the quality factors, tenderness and juiciness. Studies were made of the effects of heat, freezing and thawing before aging, beating (as with a feather-picking machine), and electrical stimulation on muscle that was free to contract or that was held under restraint. Electrical stimulation caused contraction to 70% of the original length, thaw rigor 40%, and heating or beating plus heating 50%. Much greater loss of the ultimate structural elements of the muscle was observed for muscles treated and allowed to contract than for those treated in restraint. Local contraction was noted in muscle heated under restraint, resulting in a stretching and tearing of the filamentary structure in adjacent areas.

In studies of fundamental changes in the muscle proteins that are related to tenderization during aging, it has been confirmed that collagen does not change. In breast muscle, a marked decrease occurred in the 6-24 hour post mortem period in extractable myosin, and correspondingly an increase in actomyosin extractability. This may be due to release of actin from the bound state, possibly involving breakage of bonds with tropomyosin at the Z line (i.e. junction of two sarcomeres or recurring structural units). Amounts of sarcoplasmic fraction (soluble in dilute

salt solution) and nonprotein nitrogen did not change significantly in 24 hours post mortem.

In order to have a basis for comparison of objective shear force measurements from different sized muscles or muscle slices, the relation of shear force to cross sectional area of the sheared muscle specimen was determined. Shear force was not proportional to the area as some people assume, but to approximately the 0.6th power of the area. Force thus increases more nearly in proportion to increase in a linear dimension, such as the diameter. This should have significance in explaining the basic nature of the forces resisting shearing or biting action.

C. Technology--Process and Product Development

1. Better Freeze-Dried Poultry Meat. We have developed an objective method to measure the cohesiveness in freeze-dried and other poultry meats. Uniform cylinders of cooked muscle are cemented between circular metal plates and pulled apart in a tensile tester; the force and work required to separate the fibers are recorded. The work (force times distance) is inversely correlated with cooking time, and directly correlated with undegraded collagen, the protein which binds muscle fibers together. The work required to separate fibers is significantly less for freeze-dried meat than for frozen meats. Loss of cohesiveness is due to changes that occur in the later stages of drying -- when moisture is below 30%.

The design of continuous freeze-drying equipment is investigated to help develop economical, stable, dehydrated poultry meat and to improve drying apparatuses. One result of this study is a rotating vacuum freeze drier designed for the continuous freeze-drying of small particle sized foods. A contract to acquire engineering data needed for economical freeze-drying of poultry meat was placed with the University of California, Berkeley. Thermal conductivity, pore size, bulk diffusivity and rate-limiting factors have been determined. Measurements support a mathematical model of a uniformly retreating ice front for 80% of the drying cycle. Thermal conductivity can be calculated from observed drying rates. If the pressure is cycled with helium between 1 and 10 mm. of mercury, thermal conductivity of the dry material is momentarily improved by convective heat transfer of the gas space within the piece, and the temperature of the ice core is kept low by rapidly reducing the pressure before melting occurs. By using low-density gas, good heat-transfer is provided without mass-transfer inhibition. We tested this idea by flowing a stream of low-pressure gas through the drying bed and a condenser, across a heater, through a desiccant, and back into the drying sample.

PUBLICATIONS -- USDA AND COOPERATIVE PROGRAMS

Flavor

- Klose, A. A., Palmer, H. H., Lineweaver, Hans, and Campbell, A. A. 1966. Direct olfactory demonstration of fractions of chicken aroma. J. Food Sci. 31(4):638-42.
- Pippen, Eldon L. 1967. Poultry Flavor. In "Chemistry and Physiology of Flavors," H. W. Schultz et al., eds., Avi Publishing Company, Westport, Conn., pp. 251-66.

Color, Texture and Other Quality Factors

- de Fremery, D. 1966. Some aspects of postmortem changes in poultry muscle. In "The Physiology and Biochemistry of Muscle as a Food," E. J. Briskey and others, eds., pp. 205-12, Univ. of Wisconsin Press, Madison.
- Scholtyssek, S. and Klose, A. A. 1967. The measurability of poultry meat properties. Die Fleischwirtschaft 47(1):44-5; English translation pp. 44-45.

Technology--Process and Product Development

- Bele, Linda May, Palmer, Helen H., Klose, Alvin A., and Irmiter, Theodore F. 1966. Evaluation of objective methods of measuring difference in texture of freeze-dried chicken meat. J. Food Sci. 31(5):791-800.
- Kaufman, V. F. and Rockwell, W. C. 1967. Freeze-drying apparatus. U.S. Patent No. 3,308,552.
- Rockwell, W. C., Kaufman, V. F., and Lowe, E. 1967. Continuous freeze-drying apparatus. U.S. Patent No. 3,303,578.
- Sandall, Orville C., King, C. Judson, and Wilke, C. R. 1967. The relationship between transport properties and rates of freeze-drying of poultry meat. Amer. Inst. Chem. Engin. Journal 13(3):428-38. (Contract)
- Triebes, Thomas A. and King, C. Judson. 1966. Factors influencing the rate of heat conduction in freeze-drying. I&EC Process Design and Development 5:430-6. (Contract)

AREA NO. 14. EGG UTILIZATION - FOOD

Problem. Between 1956 and 1966 egg production increased from 61 to 66 billion eggs, but per capita consumption decreased to 85% of the 1956 value. The decrease in per capita consumption reflects a decrease in table egg use. The per capita use of egg products, eggs removed from the shell and further processed is estimated to have increased during the past decade. Egg product use amounts to about 10% of the total consumption. The increase in egg product use and the consumer demand for convenience foods indicate that further efforts to increase egg product consumption will help to reverse the downward per capita trend of egg consumption.

Processing and preservation frequently alter the useful properties of eggs so that they have a reduced value for their many essential uses in baked and other prepared products. The foaming, coagulating, emulsifying and flavor properties that make eggs so valuable in bakery products must be retained in eggs that are preserved in stable forms such as frozen and dehydrated products. Therefore, the long-term objective of egg product research is to preserve and enhance at minimum cost the foaming, coagulating, emulsifying, and binding properties of eggs that make them uniquely useful in cakes, custards, puddings, souffles, omelets, meringues, pies, pancakes and other foods. The properties vary with processing treatments such as freezing, drying, homogenization, and pasteurization and also with storage. The variations are due to variable changes in one or more of the 20 plus major components of eggs. Important components include glycoproteins, lipoproteins, unconjugated proteins, free lipids, glucose, and enzymes. Interactions occur between components. Individual components exhibit damage or change in processing. Knowledge of both the properties of individual components and their interactions is needed to maximize the value of egg products in convenient and attractive forms for the consumer and therefore to increase the return available to the egg industry.

USDA AND COOPERATIVE PROGRAMS

In the Western Utilization Research and Development Division, a broad program of basic and applied research is conducted at the Division headquarters at Albany, California; by contracts and grants in Ames, Iowa, Ithaca, New York, Jefferson City, Missouri, and Davis, California; and by grant funds under P.L. 480 in India. Fundamental research is conducted on egg proteins and their relations to the functional properties and quality of eggs, on egg lipids and lipoproteins and other components of eggs. At present applied research concerns primarily the occurrence of Salmonella in eggs and egg products, methods of destroying Salmonella, and the effect of pasteurizing methods on the usefulness of egg products. Past and continuing objectives include the stabilization of yolk-containing solids for use in mixes and other convenience foods, the development of more readily

dispersible dry products, and the development of useful information on the effect of other food components (sugar, salt, whipping aids, etc.) on the properties of egg products of all types.

The Federal program of research in this area totals 12.3 scientist man-years, including contracts and grants. Of this number 4.0 are assigned to chemical composition and physical properties; and 8.3 to microbiology and toxicology. In addition, one research grant is supported by P.L. 480 funds.

PROGRAM OF STATE EXPERIMENT STATIONS

A total of 25.0 scientist man-years is devoted to research on new and improved poultry and egg products.

A. Chemical Composition and Physical Properties

1. Improved Egg Products. We are studying the physical and chemical properties of those proteins and other egg components that affect or possibly influence the functional properties of egg products. The proteins currently being investigated are ovomucin, flavoprotein, "line 18," ovoinhibitor, and the globulins of egg white.

The proteinase inhibitor activity (ovoinhibitor) of egg white was found to consist of at least three components. Their properties are being studied. We have purified the globulin, "line 18" and begun a study of its physical properties. The fractionation procedures developed led to recognition of GDP-mannose and UDP-N-acetylgalactosamine sulfate as the principal nucleotides of egg white. A UTP-diphosphahydrolase was found in egg white.

Damage to whipping properties of egg white caused by pasteurization is partially due to heat denaturation of the lysozyme-ovomucin electrostatic complex. The rate of reaction increases with pH and is proportional to the ovomucin and lysozyme concentration. The product, a denatured aggregate, decreases the mechanical stability of egg white foams.

Ultraviolet absorption and fluorescence studies of ovomucoid give strong circumstantial evidence for intramolecular tyrosylcarboxylate ion hydrogen bonds. Ovomucoid has an expandable crevice which allows the entrance of a water molecule but not a methanol molecule at pH 3, but both are admitted at pH 7.

Contract research is underway at the Iowa State University in Ames to develop new and better products by altering the functional properties of egg white. The effects of treating egg white with oxidative reagents, coordinate bond reagents, and by acylation were determined. Treating egg white with oxidative reagents did not produce any new properties of commercial interest. However, the changes produced by hydrogen

peroxide will be investigated further because of its use in egg white pasteurization. Angel cake prepared from acylated egg whites were of poor quality. Coordinate bond reagents changed the electrophoretic properties of egg white when the concentrations were much greater than those used to improve whipping rate.

The Lincoln University in Jefferson City, Missouri, recently was awarded a grant to characterize the binding properties of ovomucin and lysozyme, an interaction that affects the whipping properties of heat-treated egg white as already indicated.

Supported by P.L. 480 funds, the Indian Institute of Science in Bangalore, India, is conducting research to determine the physico-chemical nature of changes in egg yolk components caused by freezing and thawing. The "gelled" and "soluble" protein fractions of yolk are both glycoproteins containing hexose, hexose amine, and sialic acid. The soluble fraction contains about 50% more sialic acid, which may account for its non-gelling characteristic. The effect of adding pepsin to egg yolk before freezing is being evaluated. Conditions were found under which the thawed product passed quickly through the "gelled" stage to the consistency of native yolk.

Basic investigations of lysozyme from eggs and other animal sources have been concluded at the University of Paris, France. Supported by P.L. 480 funds, this project completed the determination of the chemical structure of hen's egg white lysozyme which paved the way for a study of the relative importance of some of the amino acids and their sequences as they affect biological activity. Research was conducted to determine whether or not lysozymes from different sources exhibited different biological properties and whether or not they had different chemical structures. Results indicate that lysozymes extracted from the same organ, but from different animal species, are different, lysozymes extracted from different organs of the same animal can have either different or identical properties, and more than one lysozyme can be extracted from the same secretion.

Research supported by P.L. 480 funds at the Commonwealth Scientific and Industrial Research Organization in Ryde, Australia, has been concluded. The research concerned a unique change in ovalbumin that occurs at alkaline pH (8 to 10) and mild temperature conditions (about 50° C.). Exposure converts ovalbumin to a more heat stable form. This is of both fundamental and practical importance. Comprehensive studies of the phenomenon were undertaken. The possibility that the phenomenon is due to an interchange between an S-S bond and one of the SH bonds of ovalbumin was shown not to be the case.

B. Microbiology and Toxicology

1. Control of Salmonella in Liquid and Dried Eggs. We are conducting research to develop practical, reliable methods for Salmonella destruction in processing liquid and dried egg. A survey of the heat resistance of

300 strains of Salmonella has uncovered only one strain other than the well-known S. senftenberg 775W which has relatively high heat resistance. S. blockley 2004 has 5 times the heat resistance of S. typhimurium TM-1 and S. senftenberg 775W has about 25 times the resistance. The results of our surveys of the numbers of Salmonella in raw commercial egg products (generally less than 1 per ml.) assure that a high margin of safety is achieved in pasteurized egg products, since present pasteurization conditions are designed to kill much larger numbers. Also, since Salmonella of high heat resistance are extremely rare, the occasional detection of viable Salmonella in pasteurized dried egg products seems most likely to be the result of post-pasteurization contamination.

Our studies designed to determine why S. senftenberg 775W is much more heat resistant than other Salmonella strains have shown that S. senftenberg 775W responds in the same manner as a strain of normal heat resistance to various cultural and environmental conditions. Stationary-phase cells are more resistant than log-phase cells, growth medium is without significant effect, and growth temperatures have comparable effects on both strains.

The wide range of egg products which must now be pasteurized complicates the problem of specifying conditions that will provide equal heat treatment for all without damage to their functional properties. Additives such as sugar and salt, useful in decreasing gelation in frozen yolk-containing products, alter the viscosity of the product and thus the flow rate through the pasteurizer. Since the flow rate of egg products does not correspond to an ideal system in which the degree of turbulent and laminar flow can be calculated, we have developed two methods for measuring residence time of egg products in holding tubes. These have been found reliable in plant tests; and in most pasteurization operations, the fastest-moving portion of the egg remains in the holding tube from 0.6 to 0.8 of the average residence time. The results have been used to determine the time and temperature conditions required to give adequate heat treatment to the various egg products being pasteurized.

The addition of salt or sugar increases the heat resistance of Salmonella in egg products, but the addition of acetic acid reduces the heat resistance of yolks containing either salt or sugar. Since acetic acid (vinegar) is normally used in the manufacture of mayonnaise or salad dressing we have determined the reduction in pasteurization temperature that will produce Salmonella destruction in the acidified product equal to that at a higher temperature in the usual salt and sugar yolk. If current tests on performance of acidified pasteurized salt and sugar yolk show no alteration from normal, addition of acid to these products before pasteurization will make possible significant lowering of current pasteurization temperature requirements.

A manual has been prepared to help the egg industry supply Salmonella-free products to all users and is now being reviewed for early release. It describes treatments needed to destroy Salmonella in all products and

attempts to explain why they are necessary. It contains information about the physical and chemical properties of eggs, the microbiological factors involved in pasteurization, the accepted methods of pasteurization, and a description of desirable plant lay-out and operating guidelines. The manual will be useful as an aid in training plant personnel and in helping to coordinate the regulations for pasteurization of egg products being issued by U.S.D.A., state, and local governments.

A research grant was made to Cornell University in Ithaca, New York, to develop selective sensitive methods for determining Salmonella in egg products by studying the biochemical mechanisms of their growth on selenite-enriched media. In addition to basic information developed, it was found that modification of the differential selenite medium currently in use by increasing selenite concentration from 0.4% to 3% increased recoveries of Salmonella from samples containing low levels of contamination.

Contract research is being conducted at the University of California in Davis to evaluate potential chemical pasteurization treatments by determining the changes they cause in major and minor components of eggs. Changes in proteins and/or lipids were generally observed for all agents used. The practical significance of observed changes will be determined. Effects observed include the following: Salicylaldehyde modifies the amino groups of albumin; dialysis of the modified albumin against deionized water reverses the action. Spectral and other characteristics of the model systems, glycine and butylamine, are similar to those for salicylaldehyde reacting with serum albumin. Studies of the effect of hydrogen peroxide on yolk lipids were conducted because of a proposal to use hydrogen peroxide to pasteurize whole eggs. Under the pasteurizing conditions specified, hydrogen peroxide reacted with the phospholipid but not with the triglyceride fraction of egg lipid. The chemical change in the phospholipid has not been identified, but the stability of the phospholipid fraction to oxidative deterioration at 20° C. was decreased more than 20%. The effect of peroxide on yolk products will be studied further.

PUBLICATIONS -- USDA AND COOPERATIVE PROGRAMS

Chemical Composition and Physical Properties

- Charlemagne, Daniele and Jolles, P. 1966. Lysozymes of human leucocytes and plasma. Nouvelle Revue Francaise d'Hematologie, Tome 6(3):355-66. 1/
- Gaffield, William, Vitello, Lidia, and Tomimatsu, Yoshio. 1966. Optical rotatory dispersion of egg proteins. II. Environment sensitive side chain chromophores in conalbumin. Biochem. Biophys. Res. Commun. 25(1): 35-42.
- Previero, A., Coletti-Previero, M. A., and Jolles, P. 1966. Non-enzymatic cleavage of tryptophyl peptide bonds in peptides and proteins. II. Release of a chemically modified tryptophan residue from model peptides by a mild basic treatment. Biochim. Biophys. Acta 124(2):400-2. 1/
- Tomimatsu, Yoshio, Clary, John J., and Bartulovich, John J. 1966. Physical characterization of ovoidin, a trypsin and chymotrypsin inhibitor from chicken egg white. Arch. Biochem. Biophys. 115(5):536-44.

Microbiology and Toxicology

- Ahluwalia, Gurjit S. and Williams, Harold H. 1966. Alkaline phosphatase activity from Escherichia coli grown on selenite media. Arch. Biochem. Biophys. 117(1):192-3. (Grant)
- Cunningham, F. E., Kline, L., and Lineweaver, H. 1967. Egg white composition containing triethyl phosphate. U.S. Patent No. 3,328,175.
- Kline, Leo and Sugihara, T. F. 1966. Effects of pasteurization on egg products. Bakers Digest 40(4):40-42, 47-50.
- Kline, Leo, Sugihara, T. F., and Ijichi, K. 1966. Further studies on heat pasteurization of raw liquid egg white. Food Technol. 20(12):98-100.
- Lineweaver, Hans. 1966. Pasteurization and the functional properties of egg products. Proc. Rutgers Liquid Egg Processing Course. Atlantic City, N.J. pp. 36-46.
- Lineweaver, Hans. 1966. Pasteurization of egg whites. Proc. Meat Industry Research Conference, Chicago, pp. 78-84.
- Lineweaver, Hans, Cunningham, F. E., Garibaldi, J. A., and Ijichi, Kosuke. 1967. Heat stability of egg white proteins under minimal conditions that kill Salmonellae. USDA, ARS 74-39, p. 14.

1/ Research supported by P.L. 480 funds.

- Rizk, S. S., Ayres, J. C., and Kraft, A. A. 1966. Effect of holding condition on the development of Salmonellae in artificially inoculated hens' eggs. Poultry Sci. 45(4):825-829. (Contract)
- Rizk, S. S., Ayres, J. C., and Kraft, A. A. 1966. Disinfection of eggs artificially inoculated with Salmonellae. I. Application of several disinfectants. Poultry Sci. 45(4):764-9. (Contract)
- Sugihara, T. F., Ijichi, K., and Kline, Leo. 1966. Heat pasteurization of liquid whole egg. Food Technol. 20(8):100-7.
- The destruction of Salmonellae, a report of the Western Experiment Station Collaborators Conference. U.S. Dept. Agr. ARS 74-37, 107 pp., July 1966. Contributions from the Western Regional Research Laboratory were:
- Factors affecting the heat sensitivity of Salmonellae. John A. Garibaldi
- Re-examination of heat resistance of Salmonella typhimurium in ground chicken. Henry G. Bayne
- Heat sensitivity of 300 Salmonella isolates. Henry Ng
- Sensitivity of Salmonellae to beta and gamma energy. Hans Lineweaver
- Sensitivity of Salmonellae to UV energy. Kosuke Ijichi
- Engineering aspects of egg pasteurization. George W. Putnam
- WRRL process for pasteurizing liquid egg white. F. E. Cunningham

MISCELLANEOUS PUBLICATIONS -- USDA AND COOPERATIVE PROGRAMS

Pharmacology

- Booth, A. N., Reid, J. David, and Gumbmann, M. R. 1967. Preliminary study of possible toxic effects of carbamate finishing agents. Amer. Dyestuff Reporter 56(3):19-21.
- Booth, A. N., Gumbmann, M. R., Gagne, W. E., and Reid, J. David. 1967. A study of possible toxic effects of carbamate finishing agents. USDA, ARS-72-58, p. 17.
- Keyl, A. C., Lewis, J. C., Ellis, J. J., Yates, S. G., and Tookey, H. L. 1967. Toxic fungi isolated from tall fescue. Mycopathologia et Mycologia applicata 31(3-4):327-31.
- Wiley, Mabry. 1966. Note on the analysis for aflatoxins. J. Assoc. Off. Analyt. Chem. 49(6):1223-4.

Sugar Beets

- Ames, G. R. 1967. Process for the production of ethers of organic polyhydroxy compounds. U.S. Patent No. 3,314,936. 1/
- Ames, Geoffrey R. 1967. Surface-active compositions containing mixtures of mono- and di-alkyloxymethyl ethers of sugar. U.S. Patent No. 3,300,413. 1/
- Avigad, Gad. 1966. Inhibition of glucose 6-phosphate dehydrogenase by adenosine 5'-triphosphate. National Acad. Sci. Proc. 56(5):1543-1547. 1/
- Avigad, G. 1966. Preparation of 6-³H-D-galactosides, 6-³H-D-galactose, 5-³H-D-fructose and 5-³H-L-sorbose. Israel Chemical Soc. Proc. and Israel Jour. of Chemistry Vol. 4. 1/
- Avigad, G. 1967. Synthesis of D-galactose-6-t and D-galactosides-6-t. Carbohydrate Res., 3:430-434. 1/
- Bauer, Sh. and Avigad, G. 1966. Chromatographic separation of the ring forms of reducing sugars. Israel Chem. Soc. Proc. and Israel J. Chem., Vol. 4. 1/
- Goodban, Alan E. and McCready, Rolland M. 1965. Liming of sugar beet cosettes. J. Amer. Soc. Sugar Beet Technol. 13(7):566-72.
- Katan, Rivka and Avigad, Gad. 1966. NADP dependent oxidation of TDP-glucose by an enzyme system from sugar beets. Biochem. Biophys. Res. Commun. 24(1):18-24. 1/

- Katan, Rivka and Avigad, G. 1965. The soluble nucleotides pool of the sugar beet root. Israel J. Chem. 3(4a):110. 1/
- Lowe, E., Stark, J. B., and Schultz, W. G. 1967. Engineering analysis of ion exclusion for sucrose recovery from beet molasses. Part II. Data analysis and cost projection. International Sugar Jour. 69:104-107.
- McCready, R. M. and Goodwin, J. C. 1966. Sugar transformations in stored sugar beets. J. Amer. Soc. Sugar Beet Technol. 14(3):192-205.
- McCready, R. M. 1966. Polysaccharides of sugar beet pulp; a review of their chemistry. J. Amer. Soc. Sugar Beet Technol. 14(3):260-70.
- McCready, R. M., Stark, J. B., and Goodban, A. E. 1966. Preparation of galactinol and myoinositol from sugar beet sirup by chromatography on a cation exchange resin. J. Amer. Soc. Sugar Beet Technol. 14(2):127-32.
- McCready, R. M., Goodban, A. E., Ratner, Rachel, and Ulrich, Albert. 1966. Sugar beet and purified juice quality in relation to non-sugar constituents. J. Amer. Soc. Sugar Beet Technol. 14(2):91-96.
- Schultz, W. G., Stark, J. B., and Lowe, E. 1967. Engineering analysis of ion exclusion for sucrose recovery from beet molasses. Part 1. Experimental procedures and data reduction techniques. Internatl. Sugar Jour. 69(818)35-38.
- Walker, H. G., Jr. and McCready, R. M. 1966. Some substances adsorbed on granular carbon from beet thick juice. J. Amer. Soc. Sugar Beet Technol. 14(2):142-46.

Replacement Crops

- Goldblatt, L. A. and Knowles, R. E. 1966. Dehydration of lesquerolates. U.S. Patent No. 3,291,816.
- Nelson, Jane S. and Applewhite, Thomas H. 1967. Some new derivatives of lesquerolic acid. Jour. Amer. Oil Chemists Soc. 44(5):305-306.
- Tallent, W. H., Harris, Jeanne, Wolf, I. A., and Lundin, R. E. 1966. (R)-13-hydroxy-cis-9, trans-11-octadecadienoic acid, the principal fatty acid from Coriaria nepalensis wall. seed oil. Tetrahedron Letters No. 36:4329-34.

Line Project Check List -- Reporting Year July 1, 1966 to June 30, 1967

Work & Line Project Number	Work and Line Project Titles	Work Locations During Past Year	Line Proj. Incl. in	
			Summary of Progress	Area & Subheading
W1 2-27 (Rev.)	Wheat feed products	Albany, Calif.	Yes	2-A-1
W1 2-29 (Rev.) ^{1/}	Bread flavors	Albany, Calif.	Yes	1-B-1
W1 2-43 (Rev.)	Gluten foods	Albany, Calif.	Yes	1-E-1
W1 2-44(Rev)	Protein interactions	Albany, Calif.	Yes	1-E-2
W1 2-48 (C) ^{1/}	Identification of wheat proteins by radiotracer techniques	Albany, Calif. Pullman, Wash.	Yes	1-C-1
W1 2-49 (C) ^{1/}	Protein and lipid composition of spring and winter wheat	Manhattan, Kansas	Yes	1-C-1
W1 2-50	Mechanism of flour maturation	Albany, Calif.	Yes	1-A-1
W1 2-51 ^{1/}	Compositional factors of wheat relative to continuous-mix processes	Albany, Calif.	Yes	1-C-1
W1 2-52 (C)	Wheat bran and aleurone pigments	Corvallis, Oregon	Yes	1-E-2
W1 2-53 ^{1/}	Protein-rich fractions from mill run	Albany, Calif.	Yes	1-E-1
W1 2-54 ^{1/}	Light-colored bulgur for specific markets	Albany, Calif.	Yes	1-E-2
W1 2-55 (Gr.)	Oxidation-reduction enzymes	Madison, Wisconsin	Yes	1-A-1
W1 2-56 (C)	Rheological study of doughs	Menlo Park, Calif.	Yes	1-C-1
W1 2-57 (C)	Carrying capacity of HRW wheats	Manhattan, Kansas	Yes	1-C-2
W1 2-58 (C)	Protein changes during malting	St. Paul, Minnesota	Yes	1-A-2
W1 2-59 (C)	Macromolecular structures of flour	Chicago, Ill.	Yes	1-C-1
W1 2-62 (C)	High protein rice flour	Berkeley, Calif.	Yes	3-A-1
W1 2-63	Rice product developments	Albany, Calif.	Yes	3-A-1
W1 2-64	Wheat starch effects on baking quality	Albany, Calif.	Yes	1-C-1
W1 3-16 (Rev.2)	Improved forage feed products	Albany, Calif.	Yes	4-A-1
W1 3-18 ^{1/}	Phenolic components of forages	Albany, Calif.	Yes	4-A-2
W1 3-19 (C) ^{1/}	Autooxidation of alfalfa lipids	Berkeley, Calif.	Yes	4-A-1
W1 3-20 (C)	Products from southeastern grasses	Tifton, Georgia	Yes	4-A-1
W1 3-21 (C)	Alfalfa products	Lincoln, Nebr.	Yes	4-A-1
W2 2-22 (Rev.)	Chemical treatment of wool for shrink resistance and other "easy-care" properties	Albany, Calif.	Yes	5-A-2
W2 2-24 (Rev.)	Effect of fabric construction and functional properties	Albany, Calif.	Yes	5-B-1
W2 2-28 (Rev.)	Mechanical behavior of wool fibers and fibrous assemblages	Albany, Calif.	Yes	5-A-1
W2 2-29 (Rev.) ^{1/}	Effects of radiation on natural and modified wools	Albany, Calif.	Yes	5-A-1
W2 2-32 ^{1/}	New types of yarns and fabrics from coarse wools	Albany, Calif.	Yes	5-B-2
W2 2-37 (C) ^{1/}	High luster wool fabrics	Washington, D.C.	Yes	5-A-2
W2 2-38 (C)	High energy radiation of wool	Durham, North Carolina	Yes	5-A-1
W2 2-39	Functional blends of wool with other fibers	Albany, Calif.	Yes	5-B-2
W2 2-40	Physical and chemical structure of wool	Albany, Calif.	Yes	5-A-1
W2 2-41 (C)	Oil, water, and hydrocarbon repellents	Washington, D.C.	Yes	5-A-2

^{1/} Project discontinued during the reporting period.

Line Project Check List -- Reporting Year July 1, 1966 to June 30, 1967

Work & Line Project Number	Work and Line Project Titles	Work Locations During Past Year	Line Proj. Incl. in	
			Summary of Progress	Area & Subheading
W2 2-42	WURLAN improvements	Albany, Calif.	Yes	5-A-2
W2 2-43	Ozone and electrical discharge treatments	Albany, Calif.	Yes	5-A-1
W3 1-117 (Rev.) ^{1/}	Fruit pigments	Albany, Calif.	Yes	7-C-2
W3 1-121 ^{1/}	Heat transfer surface fouling	Albany, Calif.	Yes	9-C-1
W3 1-123 (C) ^{1/}	Fruit leucoanthocyanins	Los Angeles, Calif.	Yes	7-C-2
W3 1-125	Composition of desert grapefruit	Pasadena, Calif.	Yes	6-C-2
W3 1-126	Viniferous grape products	Albany, Calif.	Yes	7-E-1
W3 1-127	New fruit dehydration methods	Albany, Calif.	Yes	7-E-2
W3 1-128 ^{1/}	Rancidity control in walnuts	Pasadena, Calif.	Yes	7-A-2
W3 1-129 (C) ^{1/}	Grape juice extraction	Davis, Calif.	Yes	7-E-1
W3 1-130 ^{1/}	Date composition and products	Pasadena, Calif.	Yes	6-A-2
W3 1-131	Tropical fruit products	Honolulu, Hawaii	Yes	6-C-1
W3 1-132	Processing quality--Northwest fruits	Puyallup, Wash.	Yes	7-E-3
W3 1-133 (C)	Products from desert grapefruit	Tucson, Ariz.	Yes	6-C-2
W3 1-134 (C)	Phenolics in canned apple juice	Fort Collins, Colo.	Yes	7-C-1
W3 1-135	Grape product developments	Albany, Calif.	Yes	7-E-1
W3 1-139	Composition of lemons and lemon products	Pasadena, Calif.	Yes	6-A-1
W3 1-140 (C)	Improvement of canned ripe olives	Berkeley, Calif.	Yes	7-B-2
W3 1-141 (C)	Determination of bitter components in navel orange products	South Pasadena, Calif.	Yes	6-B-1
W3 1-142 (C)	Improved fining methods for wine	Geneva, N. Y.	Yes	7-E-1
W3 1-143 (C)	Fluidized bed drying	Chicago, Ill.	Yes	7-E-4
W3 1-144	Navel orange bitterness	Pasadena, Calif.	Yes	6-B-2
W3 1-145 (C)	Mechanically harvested dates	Riverside, Calif.	Yes	6-C-3
W3 1-146	Flavor of fruit products	Albany, Calif.	Yes	7-B-1
W3 1-147	Dried fruit products and processes	Albany, Calif.	Yes	7-D-1
W3 1-148 (C)	Improved grapefruit products	Tucson, Ariz.	Yes	6-C-2
W3 1-149	Processing mechanically harvested dates	Albany, Calif.	Yes	6-C-3
W3 1-150	Food processing wastes	Albany, Calif.	No ^{2/}	
W3 1-151	Anthocyanins and carotenoids	Albany, Calif.	Yes	7-C-2
W3 4-80 ^{1/}	Effects of processing operations upon texture of frozen vegetables	Albany, Calif.	Yes	9-C-2
W3 4-83 ^{1/}	Mechanism of anhydration in bacterial spores	Albany, Calif.	Yes	9-D-1
W3 4-84 (C) ^{1/}	Histological studies of vegetables for dehydration	Davis, Calif.	Yes	9-E-1
W3 4-86 ^{1/}	Chemistry and enzymology of vegetable flavors	Albany, Calif.	Yes	9-B-1
W3 4-87 (C)	Removal of radioactive fallout	Berkeley, Calif.	Yes	9-E-4
W3 4-88	Processing quality--Northwest vegetables	Puyallup, Wash.	Yes	9-E-3
W3 4-89 (C)	Dry bean and pea powder	East Lansing, Mich.	Yes	9-E-2
W3 4-90 (Gr.)	Sporulation of food spoilage bacteria	Urbana, Ill.	Yes	9-D-1
W3 4-91	Effects of processing variables on dehydrated vegetables	Albany, Calif.	Yes	9-E-1
W3 4-93 (Gr.)	Lipids in plant tissue	Davis, Calif.	Yes	8-A-1
W3 4-94	Control of microbial contamination	Puyallup, Wash. Albany, Calif.	Yes	7-D-1 9-D-2

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^{2/} Recently initiated project.

Line Project Check List -- Reporting Year July 1, 1966 to June 30, 1967

Work & Line Project Number	Work and Line Project Titles	Work Locations During Past Year	Line Proj. Incl. in	
			Summary of Progress	Area & Subheading
W3 4-95	Potato products	Albany, Calif.	Yes	8-B-1
W3 4-96	Dry bean products and components	Albany and Pasadena, Calif.	Yes	9-E-2
W3 4-98	Contamination control, dehydrated vegetables	Urbana, Ill.	Yes	9-D-2
(C)				
W3 4-99	Spores as related to canned vegetables	Albany, Calif.	Yes	9-D-1
W3 4-100	Texture of frozen vegetables	Albany, Calif.	Yes	9-C-2
W3 4-101	Consistency of tomatoes	Albany, Calif.	Yes	9-E-5
W4 3-1	Chemical derivatives of ricinoleic acid	Albany, Calif.	Yes	12-A-1
(Rev.)				
W4 3-2	Foamed polyurethanes from castor oil	Albany, Calif.	Yes	12-B-1
(Rev.) ^{1/}				
W4 3-8	Castor pomace deallergenation	Albany, Calif.	Yes	11-A-1
W4 3-10	Antioxidants of safflower oil	Tucson, Ariz.	Yes	10-A-1
(C)				
W4 3-11	Polymerization of vegetable oil-derived monomers	Tucson, Ariz.	Yes	12-B-1
(C)				
W4 3-12	Continuous production of urethane foams	Minneapolis, Minn.	Yes	12-B-1
(C) ^{1/}				
W4 3-13	Stability of safflower oil	Albany, Calif.	Yes	10-A-1
W4 3-14	Food and feed products from safflower meal	Albany, Calif.	Yes	10-A-2 11-A-2
W4 3-15	Urethane polymers from castor oil	Albany, Calif.	Yes	12-B-1
W6 1-60	Histological study of frozen poultry	Madison, Wisc.	Yes	13-B-1
(C) ^{1/}				
W6 1-61	Elimination of Salmonella in egg products	Albany, Calif.	Yes	14-B-1
W6 1-62	Freeze-dried poultry meat	Albany, Calif.	Yes	13-C-1
W6 1-64	Salmonella metabolism	Ithaca, New York	Yes	14-B-1
(Gr.)				
W6 1-65	Freeze drying of poultry meat	Berkeley, Calif.	Yes	13-C-1
(C)				
W6 1-66	Pasteurization of eggs	Davis, Calif.	Yes	14-B-1
(C)				
W6 1-68	Egg proteins	Albany, Calif.	Yes	14-A-1
(Rev.)				
W6 1-69	Chemical, physical or enzymic modification of egg white	Ames, Iowa	Yes	14-A-1
(C)				
W6 1-70	Heat resistance of Salmonella	Albany, Calif.	Yes	14-B-1
W6 1-71	Microstructure of poultry meat	Madison, Wisc.	Yes	13-B-1
(C)				
W6 1-72	New and improved meat emulsion--sausage products	Lincoln, Nebr.	No ^{2/}	
(C)				
W6 1-73	Poultry muscle proteins	Albany, Calif.	Yes	13-B-1
W6 1-74	Cooked poultry aroma	Albany, Calif.	Yes	13-A-1
W6 1-75	Antioxidants to stabilize poultry products	Albany, Calif.	Yes	13-A-1
W6 1-76	Egg proteins--lysozyme and ovomucin	Jefferson City, Missouri	Yes	14-A-1
(Gr.)				
WU-P-1	Plant enzymes	Albany, Calif.	Yes	7-A-1
WU-O-0-	Fallout shelter foods	Albany, Calif.	Yes	1-B-2
2(OCD)				
WU-O-0-	Flavor components of hop oil	Albany, Calif.	Yes	9-B-2
3(BA)				
UR-A7-	Toxicity of fungal metabolites	Madras, India	No ^{3/}	
(10)-97				
UR-A10-	Rheology of wheat flour doughs	Haifa, Israel	No ^{4/}	
(10)-22 ^{1/}				

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^{2/} Recently initiated project.

^{3/} No reports available.

^{4/} Research concluded, final report not available.

Line Project Check List -- Reporting Year July 1, 1966 to June 30, 1967

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			Area & Subheading	
UR-A11-(10)-20	Dough properties	Osaka, Japan	Yes	1-C-1
UR-A11-(10)-33	Rice amylopectins	Aichi, Japan	No ^{2/}	
UR-E4-(10)-4	Soluble proteins in wheat	Antwerp, Belgium	Yes	1-C-1
UR-E9-(10)-2 ^{1/}	Composition of whole wheat lipids	Paris, France	No ^{4/}	
UR-E9-(10)-7 ^{1/}	Immunochemical analysis of wheat and barley proteins	Paris, France	Yes	1-C-1
UR-E9-(10)-8 ^{1/}	Solubility of wheat gluten proteins	Montpellier, France	No ^{4/}	
UR-E9-(10)-44 ^{1/}	Ultrasonic study of wheat gluten	Paris, France	Yes	1-C-1
UR-E9-(10)-45 ^{1/}	Enzyme action in low-moisture grain	Paris, France	No ^{4/}	
UR-E15-(10)-31 ^{1/}	Wheat germ proteins	Bologna, Italy	No ^{4/}	
UR-E21-(10)-18 ^{1/}	Coenzyme role of riboflavin of wheat endosperm	Poznan, Poland	Yes	1-A-1
UR-E27-(10)-1	Pentosans of wheat	Zurich, Switzerland	Yes	1-A-1
UR-E29-(10)-38 ^{1/}	Separation of the total protein of wheat flour	St. Albans, England	No ^{4/}	
UR-E29-(10)-76	Bread dough interactions	Chorleywood, England	Yes	1-C-1
UR-01-(10)-1	Dough rheology	North Ryde, Australia	Yes	1-C-1
UR-A10-(10)-60	Estrogen-inhibitors in forages	Jerusalem, Israel	Yes	4-A-1
UR-A10-(10)-83	Alfalfa saponins	Rehovot, Israel	Yes	4-A-1
UR-E15-(10)-17	Natural antioxidants in alfalfa	Milano, Italy	Yes	4-A-1
UR-E29-(10)-52 ^{1/}	Structure of alfalfa polysaccharides	Edinburgh, Scotland	No ^{4/}	
UR-A7-(20)-15	Molecular processes in wool	Allahabad, India	Yes	5-A-1
UR-A7-(20)-58	Adsorption of selected ions to wool	Ahmedabad, India	Yes	5-A-1
UR-A7-(20)-106	Mechanical behavior of wool fibers	Kanpur, India	No ^{2/}	
UR-E10-(20)-8	X-ray diffraction patterns of wool	Aachen, West Germany	Yes	5-A-1
UR-A10-(20)-13	Chemical effects on fiber crimp stability	Jerusalem, Israel	Yes	5-A-2
UR-E26-(20)-7	Sulfur in wool keratins	Stockholm, Sweden	Yes	5-A-1
UR-E29-(20)-56 ^{1/}	Chemical structure of wool protein	Leeds, England	No ^{3/}	
UR-A6-(30)-3	Polysaccharides in plant cell walls	Taipei, Taiwan	Yes	7-C-2
UR-A7-(30)-56	Organic acids in fruits	Baroda, India	Yes	7-C-2
UR-A7-(30)-60	Fruit leucoanthocyanins	Delhi, India	Yes	7-C-2

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Line Project Check List -- Reporting Year July 1, 1966 to June 30, 1967

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UR-A7-(30)-64	Tannin degradation in fruits	Madras, India	Yes	7-C-2
UR-A10-(30)-32	Enzymatic browning in deciduous fruits	Jerusalem, Israel	Yes	7-C-2
UR-S5-(30)-2 ^{1/}	Tropical fruit flavors	Bogota, Colombia	Yes	6-C-1
UR-E3-(30)-8	Radiation sterilization of mold contaminants	Lenaugasse, Austria	Yes	7-D-1
UR-E27-(30)-3	Enzymes in apple flavor formation	Wadenswil, Switzerland	Yes	7-B-1
UR-A7-(30)-39	Bean proteins	Allahabad, India	Yes	9-A-1
UR-E8-(10,30)-15	Composition of vegetables and fodder	Helsinki, Finland	Yes	9-B-1
UR-E9-(30)-54	Enzymatic activities of bacterial spores	Paris, France	Yes	9-D-1
UR-E26-(30)-5	Autoxidation of fats in dehydrated vegetables	Göteborg, Sweden	Yes	8-A-2
UR-E26-(30)-11	Role of metals in vegetable enzyme action	Göteborg, Sweden	Yes	8-A-1
UR-A7-(40)-21	Hydroxylated derivatives of linseed and safflower oils	Hyderabad, India	Yes	12-B-1
UR-A7-(40)-69	Polymerizable monomers from castor oil	Hyderabad, India	Yes	12-B-1
UR-A7-(40)-107	Conversion of castor oil monoglycerides	New Delhi, India	Yes	12-B-1
UR-A7-(60)-27	Physicochemical properties of hen egg yolk proteins caused by freezing	Bangalore, India	Yes	14-A-1
UR-E9-(60)-76 ^{1/}	Chemistry of egg lysozyme	Paris, France	Yes	14-A-1
UR-O1-(60)-4 ^{1/}	Ovalbumin in eggs	Ryde, New South Wales, Australia	Yes	14-A-1

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